Summary

This work is dealing with the utilization of biomass feed stocks and wooden residue for gasification process to produce the syngas which is suitable for the implementation of power plants for electricity generation and gas production problems for further chemical and energy purposes discussing the practical purification methods, given that the complexity of both theme and project which carried out through detailed analysis.

Since the obtained gas has many types of unwanted contaminants, it was necessary to derive an effective cleaning method for gas purification from chemical contaminants especially tars components.

The discussion of the definitions and methods for the determination of gas unwanted components and their removal technologies on the basis of the knowledge of data collecting and analysis, carried out through an experimental massive approach. The theoretical analysis of the gasification process for an effective tar reduction in the produced gas has been studied as well.

Since the quality requirements for internal combustion engines, gas turbines and fuel cells using the primary measurement methods cannot be achieved for gas production, this work aimed removing different particulates and tar. The main emphasis is placed on the methods of high cleaning taking in account the chemical and thermal specifications of the gas which is based on the utilization of three different kinds of carbon materials successfully and efficiently; char coal, black coke and active carbon, for tar removal which has a major impact on the process parameters. The analysis was responding with the mechanism and the techniques of minimizing the resultant allowable concentration using suitable materials and verifying the operation conditions without affecting the gas thermal efficiency.

The highlights of the theoretical and experimental work has been drawn up by a high concept cleaning allowing the production of a pure gas having a quality that meets the modern technical requirements for electricity generation.

Functionality the most efficient cleaning methods were based in the current project for tar reduction on the quantity of tar removed, the materials used for tar cracking and the conditions of the experimental work as well.

For a successful industrial application, some proposals have been settled for the improvement of gas cleaning.

Key words: Biomass gasification, gas purification, carbon materials, tar removal.

Bibliographical citation

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Declaration of Authorship

I declare that this thesis [Purification of producer gas in biomass gasification using carbon materials] and the work presented in it are my own and have been generated by me as the result of my own original research.

Signed: ………………….

Date: ………………………….

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1. Introduction

The essence of gasification process is the conversion of solid carbon fuels into carbon monoxide by thermochemical process. The gasification of solid fuel is accomplished in air sealed, closed chamber, under slight suction or pressure relative to ambient pressure.

Gasification uses heat, pressure, and steam to convert any feedstock that contains carbon (carbonaceous) into synthesis gas - a gaseous mixture composed primarily of carbon monoxide (CO) and hydrogen (H_2). Carbon monoxide and hydrogen are colorless, odorless, highly flammable gases that can be used to create electricity, chemicals, pure hydrogen, and liquid transportation fuels. Gasification systems also increasingly are being used to turn feedstock, such as coal and biomass into useful chemical products.

There are five main advantages or benefits of gasification technology.

- Feedstock flexibility
- Product flexibility
- Near-zero emissions
- High efficiency
- Energy security

1.1 The Current Status of Gasification Technology

There are close to 64 gasification equipment manufacturers all over the world quite a number of those manufacturers have just produced few units, which are still in experimental stages. In U.S.A alone there are (27) manufacturers, about 13 Universities and USDA (United states Department of Agriculture) research stations working on various aspects of biomass gasification.

The world’s largest gasification manufacturing facility is Gasifier and Equipment Manufacturing Corporation (GEMCOR) in Philippines. They produce about 3000 units / year ranging in size from 10 - 250 kW. Besides they have recently started producing gasifiers for direct heat applications. Brazil is another country where large scale gasification manufacturing program has been undertaken. About 650 units of various sizes and applications have been installed (4).

In Europe there are many manufacturers especially in Sweden, France, West Germany and Netherlands who are engaged in manufacturing gasification systems for stationery applications. Most of market for these European manufacturers has been in the developing countries.

In the U.S. and North American manufacturing activities are in the research area, the most active program in gasification is at University of California, Davis and University of Florida. Many systems in the range of 10 - 100 kW have been developed at Davis. U.S.A also is ahead of the rest of world in direct heat application gasifiers. Both fluidized and fixed bed gasifiers have been developed for this purpose (9).

In other countries of Asia and Africa the work is being carried out in research institution and few prototypes have been made and tested. Interestingly enough no mention of Japan is there in any worldwide gasification literature. However if the gasification technology does pick up it will be only a matter of time before Japan flexes its economic muscle and mass produces the gasifiers at cheaper rates.

Most of the gasifiers (up to 100 kW range) being sold by different manufacturers show a leveling off price of $ 380/ kW*e* for plant prices and about $ 150 kW*e* for basic gasifier price. This leveling off comes at about 100 kW system. However, for small systems the prices are extremely high. To this must be added the transportation costs (especially for shipment to developing countries). These prices therefore can make the gasifiers uneconomic. This explains the big gasifier manufacturing push being given in countries like Philippines, Brazil etc (10).

Unfortunately with all the activities going around the world the impact of gasification technology till to date on the economy has been negligible and far smaller than that of other renewable energy namely Solar. However gasification is a recently rediscovered technology and most of the development is still on learning curve.

Biomass is considered to be one of the key renewable resources of the future at both small- and large-scale levels. From the chemical point of view, the process of biomass gasification is quite complex. It includes a number of steps like:

- Thermal decomposition to gas, condensable vapors and chars (pyrolysis).
- Subsequent thermal cracking of vapors to gas and char.
- Gasification of char by steam or carbon dioxide.
- Partial oxidation of combustible gas, vapors and char. (15).

Biomass gasification already supplies 11 % of the world's primary energy consumption (27). But for three quarters of the world's population biomass is the most important source of energy. With increases in population and per capital demand, and depletion of fossil-fuel resources, the demand for biomass is expected to increase rapidly in developing countries. On average, biomass produces 38 % of the primary energy in developing countries. Biomass is likely to remain an important global source in some countries well into the next half of the century (4). A number of developed countries use this source quite substantially, e.g. in Sweden and Austria 15 % of their primary energy consumption is covered by biomass. Sweden has plans to increase further use of biomass as it phases down nuclear and fossil-fuel plants into the next decades. In the USA, which derives 4 % of its total energy from biomass (nearly as much as it derives from nuclear power), now more than 9000 MW electrical power is installed in facilities firing biomass. But biomass could easily supply more than 20 % of USA energy consumption. In other words, due to the available land and agricultural infrastructure this country has, biomass could, sustainably, replace all of the nuclear power plants without a major impact on food prices. Furthermore, biomass used to produce ethanol could reduce also oil imports up to 50% (27).

In considering the methods for extracting the energy, it is possible to order them by the complexity of the processes involved:

- Direct combustion of biomass.
- Thermochemical processing to upgrade the biofuel. Processes in this category include pyrolysis, gasification and liquefaction.
- Biological processing. Natural processes such as anaerobic digestion, (Anaerobic digestion (AD) is a treatment that composts the waste in the absence of oxygen, producing a biogas that can be used to generate electricity and heat.

1.2 Wood or wood waste

Wood or wood waste, as an opportunity fuel, is defined as any type of wood or wood-based product that can be burned to generate power. There are four categories that wood and wood waste fall into:

Figure 1.1 Forestry residue after a pine harvested operation and
Forestry residues converted to wood chips in preparation for conversion to biofuels

- Dedicated energy crops.
- Harvested wood (wood chips).
- Mill residue (bark, sawdust and planer shavings).
- Urban wood waste (treated/painted wood, yard trimmings, etc.).

In most wood and wood waste applications, the wood is dried, cut into chips, and transported to a boiler, where it is burned to produce steam that powers a steam turbine / generator. Co - firing with coal is sometimes used to increase the net heat rate of a coal-fired plant, but its effectiveness is limited due to wood’s poor grind ability. Pulverizes for coal are unable to handle high quantities of wood. Stokers and cyclone boilers are the most suited to co- firing wood and wood waste fuels as they require the least modifications.

In some cases, wood is liquefied into an Ethanol fuel or gasified. For best results with solid wood fuels, a boiler system made specifically for wood fuels should be used.

1.3 Bio-chemical composition of biomass

The chemical composition of biomass varies among species, but plants consist of about 25% lignin and 75% carbohydrates or sugars. The carbohydrate fraction consists of many sugar molecules linked together in long chains or polymers. Two larger carbohydrate categories that have significant value are cellulose and hemi-cellulose. The lignin fraction consists of non-sugar type molecules. Nature uses the long cellulose polymers to build the fibers that give a plant its strength. The lignin fraction acts like a “glue” that holds the cellulose fibers together.

Figure 1.2 Wood biochemical composition and wood chemical composition

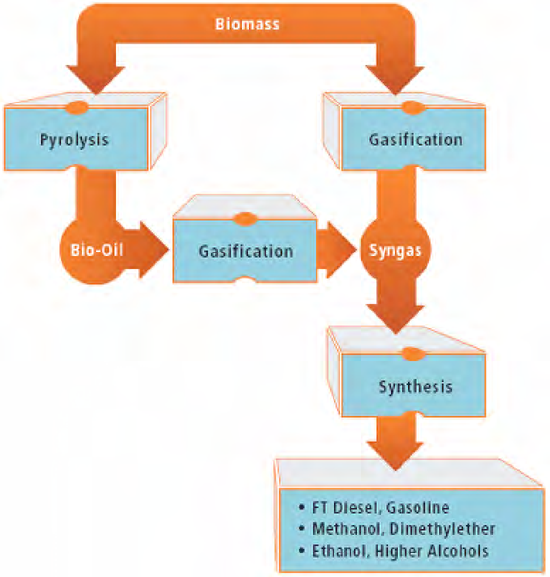


Figure 1.3 Biomass conversions routs

1.4 Proximate and ultimate analysis of biomass

Biomass fuels are characterized by what is called the "Proximate and Ultimate analyses". The "proximate" analysis gives moisture content, volatile content (when heated to 950 °C), the free carbon remaining at that point, the ash (mineral) in the sample and the high heating value (HHV) based on the complete combustion of the sample to carbon dioxide and liquid water. (The low heating value, LHV, gives the heat released when the hydrogen is burned to gaseous water, corresponding to most heating applications. Heat value of wood ranged from 18.55 - 19.56 $MJ.kg^{-1}$ of dry matter. Ager et al. (1966) studied numerous willow clones and they found water content in the interval of 50.4 to 61.7 %, whereas heat value of wood ranged from 19.0 to 20.0 $MJ.kg^{-1}$ of dry matter.

The ultimate analysis gives the composition of the biomass in *wt*% of carbon, hydrogen and oxygen (the major components) as well as sulfur and nitrogen (if any).The close relationship between the heat of combustion (high heating value, HHV) and the elemental composition as given in the ultimate analysis. This was first noticed by DuLong in the 19th century and brought up to date by other scientists.

The high heating value (HHV) is the value that is usually measured in the laboratory and would be obtained during the condensation of the water vapour into liquid water. Low heating value (LHV) is obtained when water is produced as a vapor. HHV, of typical biomass fuel will be decreased in proportion to the relation.

LHV (net) = HHV (MAF) / 1+M+A

M = Fraction of moisture (wet basis)

A = Fraction of Ash

MAF = the moisture and Ash – free basis

The Air / Biomass ratio required for total combustion is 6.27.

The LHV, can be related to the HHV and an analysis of combustion products as:

$HHV = LHV + Fm + hw$

Fm = weight fraction of moisture produced in the combustion gases

hw = the heat of vaporization of water (2257 $kJ\ kg^{-1}$)

Also it is possible to rewrite these values as below:

$Q_i = Q_s - r\,(w + 8.94H_2)$ KJ/kg

Where, Q_i =LHV, and Q_s = HHV, r = contents of water in the fuel, and H_2=Hydrogen content.

1.5 Gasification process zones

1.5.1 Drying

Biomass fuels consist of moisture ranging from 5 to 35%. At the temperature above 100 °C, the water is removed and converted into steam. In the drying, fuels do not experience any kind of decomposition. As the feedstock is heated and its temperature increases, water is the first constituent to evolve:

Moist feedstock + Heat $\longrightarrow$ Dry feedstock + H_2O

At moisture content of 87 % the energy content of the wood is the same as the required energy to evaporate the moisture. The critical limit is 50 - 55 % moisture; further increased moisture content above this level lowers the energy content dramatically, but the moisture content should not always decrease to below a certain limit, as very dry biomass produces a syngas with less H_2. Cost increases also quickly with very dry biomass.

1.5.2 Pyrolysis

Pyrolysis is the thermal decomposition of biomass fuels in the absence of oxygen. Pyrolysis as shown in Fig.1.4 involves release of three kinds of products: solid, liquid and gases. The ratio of products is influenced by the chemical composition of biomass fuels and the operating conditions.
The devolatilisation (pyrolysis) is slightly endothermic and, for temperatures above 500 °C, 75 - 90 *wt*% volatile matters are produced in the form of steam plus gaseous and condensable hydrocarbons. The relative yields of gas, condensable vapors (including tars) and the remaining char depend mostly on the rate of heating and the final temperature. A high process temperature is maintained in various ways, depending on the type of reactor.

It is noted that no matter how gasifier is built, there will always be a low temperature zone, where Pyrolysis takes place, generating condensable hydrocarbon. It was observed that commercially proven pyrolysis technology at this scale of operation is not very common.

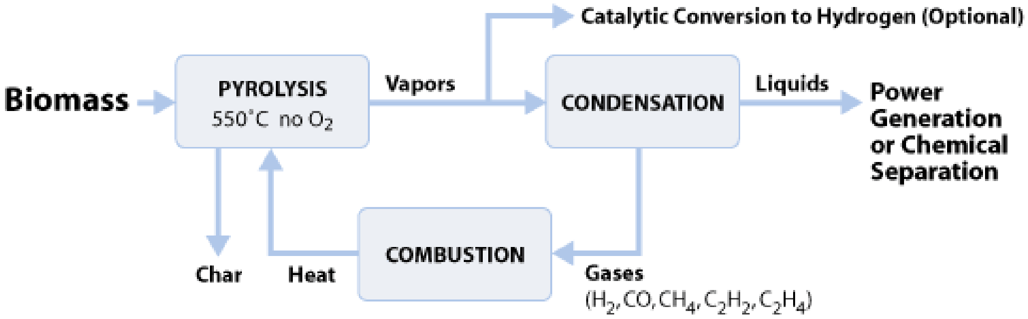


Figure 1.4 Pyrolysis Process

1.5.3 Oxidation

Introduced air in the oxidation zone contains, besides oxygen and water vapour, inert gases such as nitrogen and argon. These inert gases are considered to be non-reactive with fuel constituents. The oxidation takes place at the temperature of 700 - 2000°C. Heterogeneous reaction takes place between oxygen in the air and solid carbonized fuel, producing carbon monoxide. Plus and minus sign indicate the release and supply of heat energy during the process respectively.

1.5.4 Reduction

In reduction zone, a number of high temperature chemical reactions take place in the absence of oxygen. Heat is required during the reduction process. Hence, the temperature of gas goes down during this stage. If complete gasification takes place, all the carbon is burned or reduced to carbon monoxide, a combustible gas and some other mineral matter is vaporized. The remains are ash and some char (unburned carbon).

1.5.5 Chemical Reactions

In complete combustion, carbon dioxide is obtained from the carbon and water from the hydrogen. Oxygen from the fuel will of course be incorporated in the combustion products, thereby decreasing the amount of combustion air needed (95).

Combustion, occurring in the oxidation zone, is described by the following heterogeneous chemical reactions;

$C + O_2 \longrightarrow CO_2 + 393.8\ KJ / mol$ reaction (1)

$C + ½\ O_2 \longrightarrow CO + 123.1\ KJ / mol$ reaction (2)

Thus, burning 1 mol or 12.01 g of carbon to carbon dioxide releases a heat quantity of 393.9 KJ.

These two reactions provide the heat necessary for the endothermic reactions in the drying, pyrolysis reaction zone.

The water vapor introduced with the air production by the drying and pyrolysis of the biomass reacts with the hot carbon according to the following heterogeneous reversible water gas reaction:

$C + H_2O + 118.5\ KJ / mol \longrightarrow CO + H_2$ reaction (3)

So, for each mol of carbon 118.5 KJ is consumed to produce one mol of CO and one mol of H_2.

The most important reduction reactions are the water gas reaction (3) and the following Boudouard reaction;

$C + CO_2 + 159.9\ KJ / mol \longrightarrow 2CO$ reaction (4)

Besides these reactions several other reduction reactions take place of which the most important ones are the water shift reaction (5) and the methanisation reaction (6).

$CO_2 + H_2 + 40.9\ KJ/\ mol \longrightarrow CO + H_2O$ reaction (5)
$C + 2H_2 \longrightarrow CH_4 + 87.5\ KJ\ /\ mol$ reaction (6)

Equation (5) describes the homogenous water gas shift reaction.

$CO + ½\ O_2 \longrightarrow CO_2 + 283.99\ KJ/\ mol$ reaction (7)
$H_2 + ½\ O_2 \longrightarrow H_2O + 285.9\ KJ/\ mol$ reaction (8)

The carbon or carbon monoxide may be combusted according to equations (7) and (8), although they produce heat which is beneficial to the gasification process, they are undesirable because they reduce the heating value.

The ratio between of the concentration of carbon monoxide (CO) and water vapor (H_2O) and the concentration of carbon dioxide (CO_2) and (H_2) is fixed by the value of the water gas equilibrium constant (Kw).

$Kw = ([CO] * [H_2O])\ /\ ([CO_2] * [H_2])$ reaction (9)

1.6 Producer Gas Composition

The producer gas is the mixture of combustible and non-combustible gases. The quantity of gases constituents of the produced gas depends upon the type of fuel and operating condition.

The typical producer gas is composed of nitrogen (approximately 55% by volume), carbon dioxide (approximately 16%), carbon monoxide (12% - 30 %), and hydrogen (2% to 10%). Small percentages of light hydrocarbons, oxygen, solid particles, and tar, as well as other elements particular to the process and feed material may also be present. After separation of the solid particles, tar, and organic constituents of the gas, by gas scrubbing, the organic pollutants are transformed into simple molecules (H_2 and CO).

The heating values of producer gas vary from 4.5 - 6 MJ/m^3 depending upon the quantity of its constituents. Carbon monoxide is produced from the reduction of carbon dioxide and its quantity varies from 15 - 30 % by volume basis. Although carbon monoxide posses higher octane number of 106, its ignition speed is low.

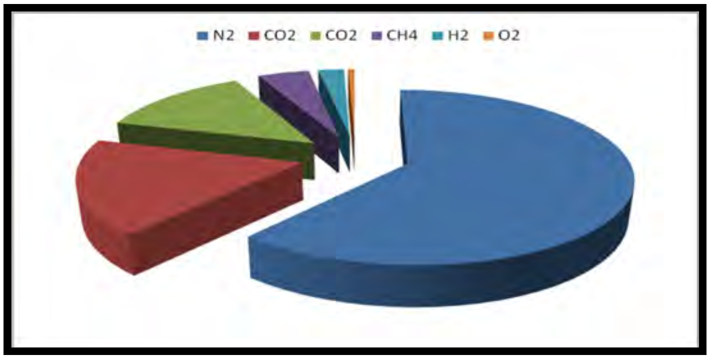


Figure 1.5 Producer gas compositions

This gas is toxic in nature. Hence, human operators need to be careful while handling gas. Hydrogen is also a product of reduction process in the gasifier. Hydrogen posses the octane number of 60 - 66 and it increases the ignition ability of producer gas. Methane and hydrogen are responsible for higher heating value of producer gas. Amount of methane present in producer gas is very less (up to 4 %). Carbon dioxide and nitrogen are non-combustible (inert) gases present in the producer gas. Compared to other gas constituents, producer gas contains highest amount (45 - 60 %) of nitrogen. The amount of carbon dioxide varies from 5 - 15 %. Higher percentage of carbon dioxide indicates incomplete reduction. Water vapor in the producer gas occurs due to moisture content of air introduced during oxidation process, injection of steam in gasifier or moisture content of biomass fuels.

1.7 Environmental Considerations

Gasification, the conversion of biomaterial into energy, offers an environmentally sound, outstanding alternative to expensive and environmentally unfavorable disposal of residual organic wastes in landfills. Wastewater treatment residuals, agricultural crop by-products, and manure represent excellent, low-cost fuel for high-efficient gasifier. The removal and use of these “waste-products” can also help to control non-point source pollution in environmentally sensitive areas. Since the gasification process uses plant and organic matter or organic residuals to generate electricity and other energy sources, the fossil fuels are in essence, simply replaced with organic matter as a fuel source, creating a cleaner, renewable energy alternative, and reducing air pollution associated with the combustion of fossil fuels. In this way, Biomass fueled energy systems offer the potential to reduce greenhouse gases and have nowhere near the global warming impacts of fossil fuel plants. Biomass fuels can be referred to as carbon dioxide (CO_2) neutral, given that the plant material absorbs as much carbon dioxide during its life as is released even if it were directly combusted. Gasification / pyrolysis technologies can capture / convert CO_2 further reducing its impact when compared to direct-burn bioenergy systems. Since biomass fuels seldom contain elevated concentrations of Sulfur compounds, SO_x emissions are often times zero or very small compared to fossil fuels.

2. Types of gasification plants

An extensive review of gasifier manufacturers in Europe, USA and Canada identified 50 manufacturers offering ‘commercial’ gasification plants from which:

75% of the designs were downdraft type.
20% of the designs were fluidized bed systems.
2.5% of the designs were updraft type.
2.5% were of various other designs. (135)

Gasifier operating conditions vary over a range of temperatures from a few hundred to over a thousand degrees Celsius, and pressures from near atmospheric to as much as 30 atmospheres. Both pressurized and atmospheric operations of gasifiers have advantages and disadvantages although gas compositions and heating values are not significantly different for either system.

- Pressurized Gasifier has the following features:
  - Feeding is more complex and very costly, as the feedstock has to be supplied at pressure.
  - The system has to be cleaned out by blowing it through (purging) with inert gas
  - Capital costs of pressure equipment are much higher than atmospheric equipment although sizes are much smaller.
  - Gas is supplied to the turbine at pressure removing the need for gas Compression before use in a gas turbine and also allowing relatively high tar contents in the gas.
  - Overall system efficiency is higher due to retention of sensible heat (i.e. that already acquired by the gas) and chemical energy of tars in the products.
- Atmospheric Gasifier has the following features:
  - For gas turbine applications the product gas is required to be sufficiently clean for compression prior to the turbine. For engine applications the gas quality requirements are less onerous and pressure is not required.
  - Atmospheric applications have a potentially much lower capital cost at smaller capacities of below around 30 MW*e*.

Changing the pressure and temperature at which the reactions take place affects the composition of the product gas. Increasing the temperature of the process (at constant pressure) increases the amounts of carbon monoxide and hydrogen produced. Increasing the pressure (at constant temperature) increases the amount of Methane produced. Methane is the main constituent of natural gas and has a HHV of 40 MJ/m^3. Of all the available gasifier types, the downdraft gasifier has received the most attention and is suited for smaller power levels (i.e. ~ 100 kW*e*). The updraft gasifier is preferred for 35 MW*e* power levels. The fluidized bed is best suited for 10 MW*e* and above.

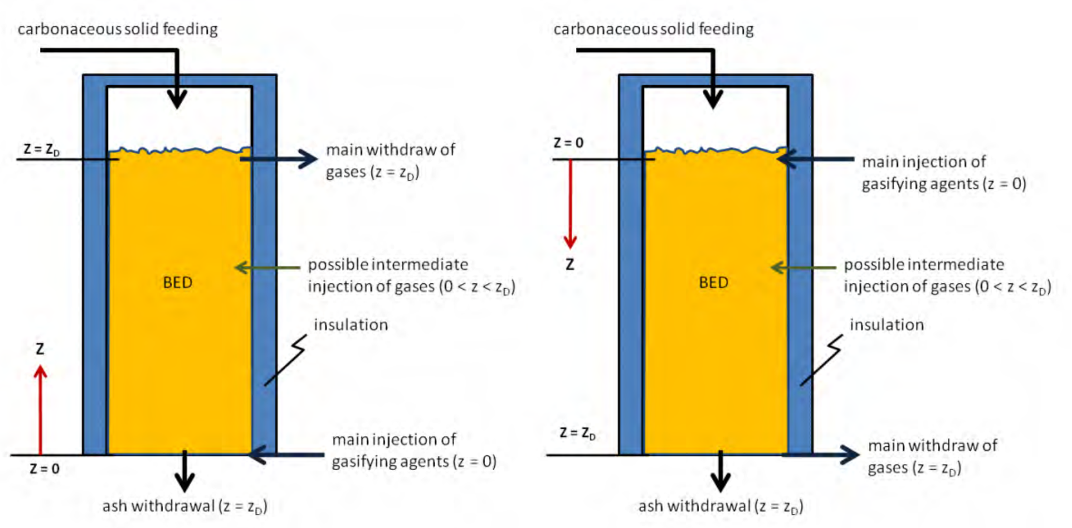


Figure 2.1 Downdraft and Updraft gasification power Plants (27)

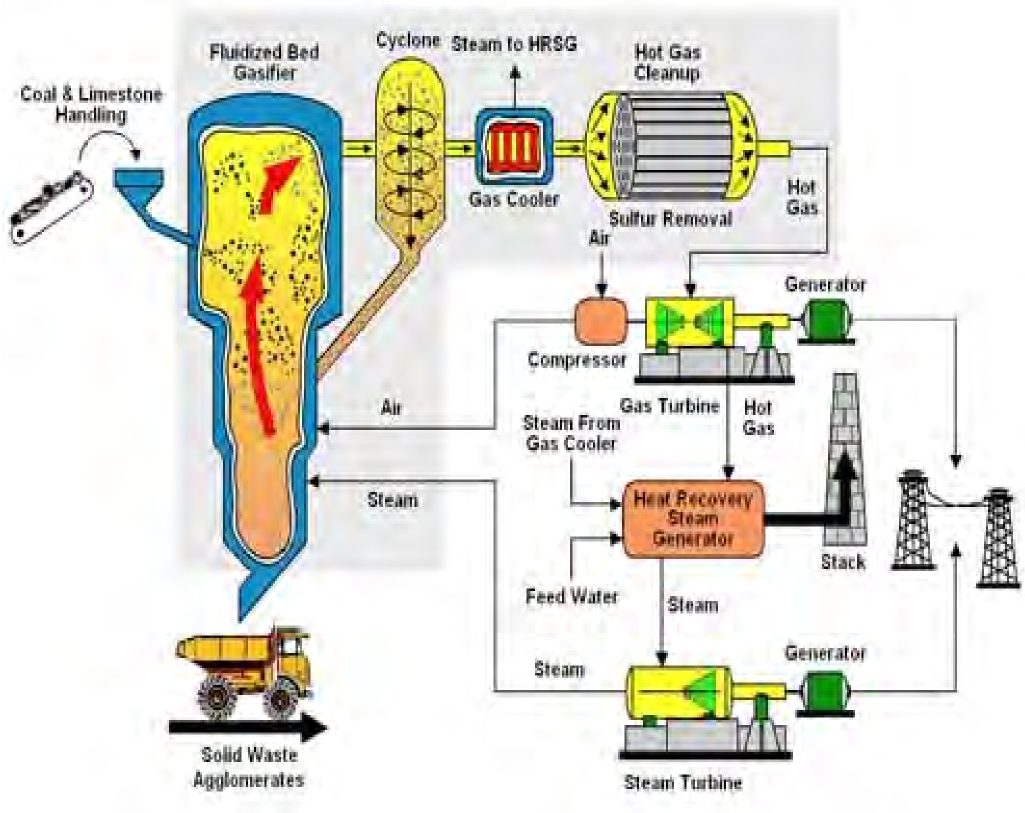


Figure 2.2 Fluidized bed gasification power plants (39)

2.1 The Updraft Gasifier

Which is the oldest type, consists of a fixed bed of carbonaceous fuel (e.g. coal or biomass) through which the "gasification agent" (steam, oxygen and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag. The throughput for this type of gasifier is relatively low and thermal efficiency is high as the gas exit temperatures are relatively low. However, tar and methane production is significant at typical operation temperatures, so product gas must be extensively cleaned before use or recycled to the reactor. These systems often are called Lurgi or Sasol gasifiers.
The common reactor configurations are outline in Table 2.1 (45).

Fixed bed gasifier	Uses a bed of solid fuel particles through which the air and gas pass either up or down. They are the simplest type of gasifiers and are the only ones suitable for small-scale application
Downdraft gasifier - The co-current fixed bed	Developed to convert high volatile fuels (wood, biomass) into low tar gas and therefore has proven to be the most successful design for power generation.
Updraft gasifier – The counter- current fixed bed	Widely used for coal gasification and non-volatile fuels such as charcoal. However, the high rate of tar production (5%-20%) makes them impractical for high volatile fuels

	where a clean gas is required.
Fluidized bed gasifiers	Favored by many designers for gasifiers producing more than 40GJ/h and for gasifiers using smaller particle feedstock sizes. In a fluidized bed, air rises through a grate covered in sand at high enough velocity to levitate the particles above the grate, thus forming a “fluidized bed”. Above the bed itself the vessel increases in diameter, lowering the gas velocity and causing particles to recirculate within the bed itself. The recirculation results in high heat and mass transfer between particle and gas stream.

Table 2.1 Common reactor configurations

2.2 The downdraft Gasifier

Is similar to the counter-current type, but the gasification agent gas flows in co-current configuration with the fuel (downwards, hence the name "downdraft gasifier"). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is transferred to the gasification agent added in the top of the bed, resulting in energy efficiency on level with the counter-current type. Since all tars must pass through a hot bed of char in this configuration, tar levels are much lower than the counter-current type. In this type of gasifier a descending packed bed of biomass is supported across a constriction known as a throat. A co - current of gases and solids flows through this bed i.e. both gases and solid flow through the gasifier in the same direction. The throat is where most of the gasification reactions occur. There is a turbulent high temperature region around the throat where the reaction products are intimately mixed. This mixing aids the tar cracking. Some tar cracking also takes place below the throat on a residual charcoal bed where the gasification is completed. This configuration is simple, reliable and proven for certain fuels and results in a high conversion of pyrolysis intermediates and hence a relatively clean gas (51).

The fuels suitable for use in this type of gasifier include relatively dry (up to about 30 % (wet basis)) blocks or lumps and containing a low proportion of fine and coarse particles i.e. not smaller than about 1cm and not bigger than 30cm in the longest dimension). The gas produced has a low content of tars. Because of this, the downdraft configuration is generally favored for small-scale electricity generation with an internal combustion engine.

The practical upper limit to the capacity of this configuration is around 50kg/h of feedstock or 500 kW*e*. The limit is set by the physical limitations of the diameter of the gasifier throat and the size of the particles.

A relatively new concept of stratified or open core downdraft gasifier has been developed in which there is no throat and the bed is supported on a grate. This was first devised by the Chinese for rice husk gasification and has subsequently been used in India.

2.3 Fluid Bed Gasifier

This type of gasifier is also referred to as a bubbling fluid bed gasifier. The air bubbling upwards through the feedstock results in a method of solid-gas contacting that has excellent mixing characteristics and high reaction rates. As the gas passes upwards through the packed bed of particles (coarse sand is commonly used) a pressure drop is formed across the bed. This pressure drop increases as the gas velocity increases until the bed of solid particles expands slightly. At this point the individual particles become supported in the gas stream with freedom of movement relative to one another. The bed is then said to be fluidized and has the appearance of a boiling liquid with a well-defined free surface. Higher gas velocities result in entrainment of the solid particles and the surface loses its well-defined interface.

Fluid bed gasifiers are the only gasifiers with isothermal bed operation i.e. the whole bed is at the same temperature. Their typical operating temperature is at 800 - 850°C.

Most of the conversion of the feedstock takes place within the bed. Some conversion does, however, continue to take place in the freeboard section above the fluid bed as some pyrolysis products are swept out of the fluid bed by gasification products. These are converted by further thermal cracking.

In most cases, carbon conversion approaches 100%. This is not the case if excessive carryover of fines takes place. This occurs with a top-feeding configuration. The gas produced by the bubbling fluid bed gasifiers tends to have a tar content somewhere between that of the updraft and downdraft gasifiers.

The bed can lose its fluidity due to sintering, which is when the solid feedstock fuses together without melting. Alkali metals from the biomass ash form low melting point substances (eutectics) with the silica in the sand of the bed. This results in the eventual loss of bed fluidity. This is quite a common problem but its occurrence depends on the thermal characteristics of the ash. The inherently lower operating temperature and better temperature control of a fluid bed provide an acceptable control measure. With biomass of high ash/inert content it is better to use alumina or even metallic sand such as chromite sand in the fluid bed itself (57).

The carbon loss with entrained ash may be significant. This means that fluidized beds are uneconomical for small-scale applications. They also incur higher operating costs. This type of gasifier can be readily scaled up. Multiple feeding is used in large beds where fuel distribution can become a problem. Alternative configurations such as twin bed systems and circulating fluidized beds are available. As a result, there are processes to suit almost every type of feedstock or thermo chemical process.

Fluidized beds can provide high rates of heat and mass transfer and good mixing of the solid phase. Relatively high reaction rates are possible and the temperature is more or less constant in the bed. The particles need to be in the range of 1 - 10 mm in diameter and so the feedstock may need to be reduced in size to meet the particle requirements of the fluidized bed. The ash is elutriated (separated by washing into coarser and finer potions) and removed as fine particles entrained in the product gas (122).

2.4 Circulating Fluid Bed (CFB)

In this type of gasifier the air velocity through the fluid bed is high. Because of this, large amounts of solids are entrained with the product gas.
The system is designed so that these solids are recycled back to the fluid bed. This improves the carbon conversion efficiency and makes it greater than that for the single fluid bed design.

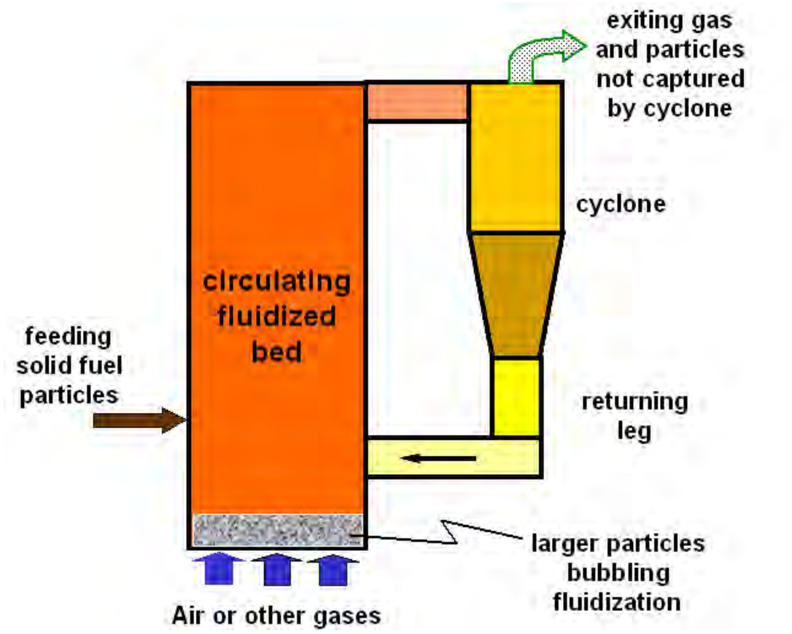


Figure 2.3 Circulating bed Gasifier

2.5 Twin Fluid Bed

The use of two fluid bed gasifiers gives a higher heating value product gas than a single air blown gasifier. It is heated with hot sand from the second fluid bed. This second fluid bed is heated by burning the product char in air before recirculation it back to the first reactor. Hydrogen is generated when a shift reaction occurs. This shift reaction occurs upon the addition of steam to the gasifier. The presence of steam also encourages carbon-steam reactions. The product gas has a fairly high heating value but contains tars from the pyrolysis process. A summary of gasifier characteristics is given in Table 2.2 compares gasification product gas characteristics (57):

Gasifier Type	Characteristics
Downdraft	Simple, reliable and proven for certain fuels, Relatively simple construction, Close specification on feedstock characteristics, Uniform sized feed required, Very limited scale-up potential, Possible ash fusion and clinker formation on the grate High residence time of solids, Needs low moisture fuels High carbon conversion, Low ash carry over, Fairly clean gas is produced, Low specific capacity.
Updraft	Product gas is very dirty with high levels of tars, Very simple and robust construction, Good scale up potential, Suitable for direct firing, High residence time of solids, Relatively simple construction, Low exit gas temperature, High thermal efficiency, High carbon conversion, Low ash carry over.
Bubbling Fluid Bed	Good temperature control, High reaction rates, In-bed catalytic processing is possible, Greater tolerance to particle size range, Moderate tar levels in product gas, Higher particulates in the product gas, Good gas-solid contact and mixing, Tolerates variations in fuel quality, Easily started and stopped, Good scale-up potential, Low feedstock inventory, Carbon loss with ash High specific capacity, Can operate at partial load.
Circulating Fluid Bed	Good temperature control and high reaction rates In-bed catalytic processing not possible, Greater tolerance to particle size range, Moderate tar levels in product gas, Relatively simple construction and operation High specific capacity, Very good scale-up potential, High carbon conversion, Good gas-solid contact.

Table 2.2 Gasifier characteristics

Also gas quality for each gasifier is given in Table 2.3:

Gasifier Type	Gas Quality	
	Tars	Dust
Fluid bed air-blown	fair	poor
Updraft air-blown	poor	fair
Downdraft air-blown	good	good
Downdraft oxygen-blown	good	fair
Multi-solid fluid bed	fair	poor
Twin fluidized bed	fair	poor
Pyrolysis (for comparison)	poor	good

Table 2.3 Gas qualities for each gasifier

3. Gasifier Fuel Characteristics

Almost any carbonaceous or biomass fuel can be gasified under experimental or laboratory conditions. However the real test for a good gasifier is not whether a combustible gas can be generated by burning a biomass fuel with 20 - 40% stoichiometric air but that a reliable gas producer can be made which can also be economically attractive to the customer. Towards this goal the fuel characteristics have to be evaluated and fuel processing done.

Many gasifiers' manufacturers claim that a gasifier is available which can gasify any fuel. There is no such thing as a universal gasifier. A gasifier is very fuel specific and it is tailored around a fuel rather than the other way round. Thus a gasifier fuel can be classified as good or bad according to the following parameters (49):

- Energy content of the fuel
- Bulk density
- Moisture content
- Dust content
- Ash and slugging characteristic
- Tar content

3.1 Energy content and Bulk Density of fuel

Energy content of fuel is obtained in most cases in an adiabatic process. The values obtained are higher heating values which include the heat of condensation from water formed in the combustion of fuel. The heating values are also reported on moisture and ash basis. Fuel with higher energy content is always better for gasification. The most of the biomass fuels (wood, straw) has heating value in the range of 10 - 16 MJ/kg, whereas liquid fuel (diesel, gasoline) posses higher heating value. The higher the energy content and bulk density of fuel, the similar is the gasifier volume since for one charge to get power for longer time. Bulk density is defined as the weight per unit volume of fuel. Bulk density varies significantly with moisture content and particle size of fuel. Volume occupied by stored fuel depends on not only the bulk density of fuel, but also on the manner in which fuel is piled. It is also recognized that bulk density has considerable impact on gas quality, as it influences the fuel residence time in the fire box, fuel velocity and gas flow rate (63).

In most fuels there is very little choice in moisture content since it is determined by the type of fuel, its origin and treatment. It is desirable to use fuel with low moisture content because heat loss due to its evaporation before gasification is considerable and the heat budget of the gasification reaction is impaired. Besides impairing the gasifier heat budget, high moisture content also puts load on cooling and filtering equipment by increasing the pressure drop across these units because of condensing liquid. Thus in order to reduce the moisture content of fuel some pretreatment of fuel is required. Generally, desirable moisture content for fuel should be less than 20%.

3.2 Dust content

All gasifier fuels produce dust. This dust is a nuisance since it can clog the internal combustion engine and hence has to be removed. The gasifier design should be such that it should not produce more than 2 - 6 g/m³ of dust. The higher the dust produced, more load is put on filters necessitating their frequent flushing and increased maintenance.

3.3 Ash and Slugging Characteristics

The mineral content in the fuel that remains in oxidized form after complete combustion is usually called ash. The ash content of a fuel and the ash composition has a major impact on trouble free operation of gasifier. Ash basically interferes with gasification process in two ways (58):

- It fuses together to form slag and this clinker stops or inhibits the downward flow of biomass feed.
- Even if it does not fuse together it shelters the points in fuel where ignition is initiated and thus lowers the fuel’s reaction response.

Ash and tar removal are the two most important processes in gasification system for its smooth running. Various systems have been devised for ash removal. In fact some fuels with high ash content can be easily gasified if elaborate ash removal system is installed in the gasifier. Slugging, however, can be overcome by two types of operation of gasifier:

- Low temperature operation that keeps the temperature well below the flow temperature of the ash.
- High temperature operation that keeps the temperature above the melting point of ash.

The first method is usually accomplished by steam or water injection while the latter method requires provisions for tapping the molten slag out of the oxidation zone. Each method has its advantages and disadvantages and depends on specific fuel and gasifier design.

Keeping in mind the above characteristics of fuel, only two fuels have been thoroughly tested and proven to be reliable. They are charcoal and wood. They were the principal fuels during World War II and the European countries had developed elaborate mechanisms of ensuring strict quality control on them. More research needs to be done in order to make gasification systems running on these fuels on a large scale (149).

3.4 Tar content

When biomass is heated the molecular bonds of the biomass break; the smallest molecules gaseous, the larger molecules are called primary tars. These primary tars, which are always fragments of the original material, can react to secondary tars by further reactions at the same temperature and to tertiary tars at high temperature. This tar formation pathway can be visualized as follows:

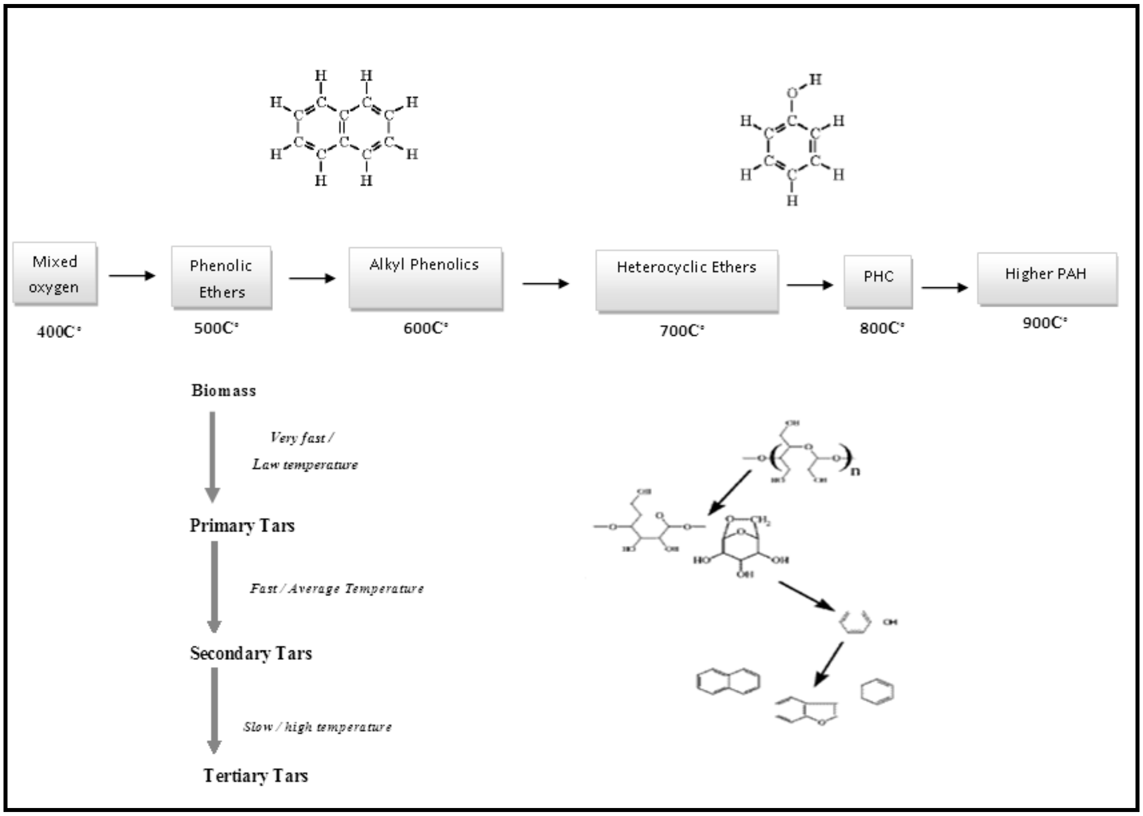


Figure 3.1 Tar formation Scheme

Tar is one of the most unpleasant constituents of the gas as it tends to deposit in the carburetor and intake valves causing sticking and troublesome operations. It is a product of highly irreversible process taking place in the pyrolysis zone. The physical property of tar depends upon temperature and heat rate and the appearance ranges from brown and watery (60% water) to black and highly viscous (7% water). There are approximately 200 chemical constituents that have been identified in tar so far.

Very little research work has been done in the area of removing or burning tar in the gasifier so that relatively tar free gas comes out. Thus the major effort has been devoted to cleaning this tar by filters and coolers. A well-designed gasifier should put out less than 1 g/m³ of tar. Usually it is assumed that a downdraft gasifier produces less tar than other gasifiers. However because of localized inefficient processes taking place in the throat of the downdraft gasifier it does not allow the complete dissociation of tar (107).

Tar classification system was defined based on the physical tar properties: water solubility of tar and tar condensation, Table 3.1 gives a description for the five tar classes in the classification system with the focus on the tar properties.

Class 1	GC undetectable tars. This class includes the heaviest tars that condense at high temperature even at very low concentrations.
Class 2	Heterocyclic components (like phenol, pyridine, and cresol). These are components that generally exhibit high water solubility, due to their polarity.

Class 3	Aromatic (1 ring) components. Light hydrocarbons that are not important in condensation and water solubility issues like xylene, styrene, toluene.
Class 4	Light polyaromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures, like naphthalene; methyl-naphthalene; biphenyl; ethenylnaphtalene; Acenaphthylene; acenaphtene; fluorene; Phenanthrene; anthracene.
Class 5	Heavy polyaromatic hydrocarbons (4-5 rings PAH's). These components condense at relatively high temperature at low concentrations like fluoranthen; Pyrene; benzo-anthracene; chrysene; benzo-fluoranthen; benzo-Pyrene; perylene; Indeno-pyrene; Dibenzo-anthracene; Benzo-perylene.

Table 3.1 Description of the tar classes with a focus on the tar properties

The type of classification division of light and heavy tar, Light tar is all tar that is measurable with a gas chromatograph; heavy tar is all the rest. Heavy tars are considered to have at most 4 to 7 aromatic rings, other tars with more aromatic rings are considered to be heavy tars (gravimetric tar). Figure 3.1 shows a global overview of tars formation Scheme and since the molecules of tertiary tar are often heavier than primary tar, methods of approach are:

- Sampling: isokinatic, high-temperature particulate filtration, tar absorption in a solvent.
- Analysis: concentration of gravimetric tar from evaporation residue at standard conditions (T, P and t)
- Analysis: concentration of individual tar compounds from GC analysis

The composition of tar depends on the gasification process. In principle tar can be divided into two groups: low temperature tar which is formed in the updraft gasifier and consist mostly of polar compounds and high temperature tar which is formed in the downdraft and fluidized bed gasifier and consist mostly of non-polar compounds (129).

For the analysis, a selection of compounds were performed which called to be most reprehensive for the composition spectrum respectively in the fluidized bed gasifier, the following compounds were selected, benzene, toluene, phenol, indane + indene, naphthalene, methylnaphthalene and fluorine. Fig. 3.2 shows the classes' distribution of tar as a function of temperature and Fig.3.3 shows the tar dew point as calculated by ECN tar dew point calculation program.

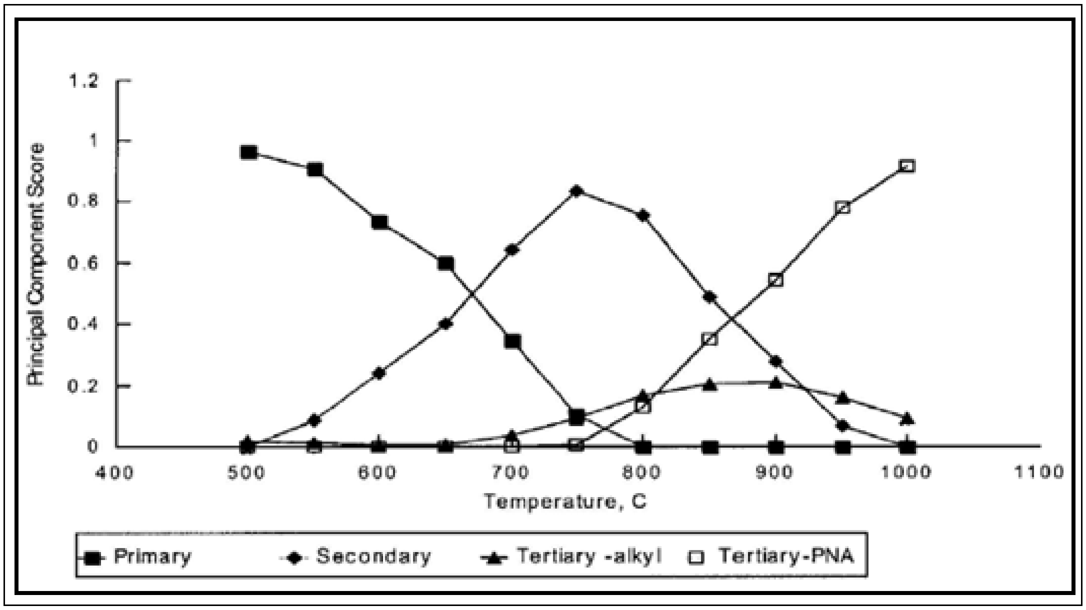


Figure 3.2 Distribution of four tar components as a function of temperature

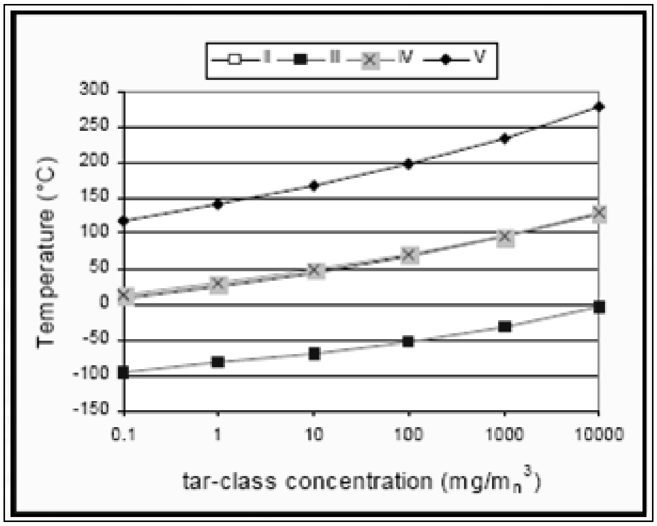


Figure 3.3 Tar dew point as calculated by ECN tar dew point calculation program

4. Gas Cleaning and Conditioning

The combustible gases from the gasifier can be used:

- In internal combustion engines,
- For direct heat applications and
- As feedstock for production of chemicals like methanol.

However in order for the gas to be used for any of the above applications it should be cleaned of tar and dust and be cooled. As previously mentioned cooling and cleaning of the gas is one of the most important processes in the whole gasification system. The failure or the success of producer gas units depends completely on their ability to provide a clean and cool gas to the engines or for burners. Thus the importance of cleaning and cooling systems cannot be overemphasized.

The temperature of gas coming out of generator is normally 300 - 800°C. This gas has to be cooled in order to raise its energy density. Various types of cooling equipment have been used to achieve this end. Most coolers are gas to air heat exchangers where the cooling is done by free convection of air on the outside surface of heat exchanger. Since the gas also contains moisture and tar, some heat exchangers provide partial scrubbing of gas. Thus ideally the gas going to an internal combustion engine should be cooled to nearly ambient temperature (134).

	Updraft	**Downdraft**	**Fluidized**
Exit temperature [°C]	80 – 250 – 400	800 – 1000	700 – 1000
Tar content [g/Nm3	10 – 100	0.1 – 5	1 – 3
Dust content [g/Nm3]	0.1 – 1	1 – 10	10
Related purification process	Particles + Hydro cracking	Particles + (Steam Reforming)	Particles + (Steam reforming)
Operation temperature purification [°C]	400 – 500	900 – 1000	900 – 1000
Tar content exit purification [g/Nm3]	0.1– 1 Hydrogenated product	0.1	0.1

Table 4.1 Typical contaminates in various gasification plants

Cleaning of the gas is trickier and is very critical. Normally three types of filters are used in this process. They are classified as dry, moist and wet. In the dry category are cyclone filters. They are designed according to the rate of gas production and its dust content. The cyclone filters are useful for cleaning particles of the size of 5 µm and greater. Since 60 - 65% of the producer gas contains particles above 60 µm in size the cyclone filter is an excellent cleaning device.

The gas after passing through cyclone filter still contains fine dust, particles and tar. It is further cleaned by passing through either a wet scrubber or dry cloth filter. In the wet scrubber the gas is washed by water in countercurrent mode. The scrubber also acts like a cooler, from where the gas goes to cloth or cork filter for final cleaning. Table 4.1 show the typical contaminates in various gasification plants.

In the Gas Cleaning and Conditioning area, the goal is to achieve near-zero emissions while simultaneously reducing capital and operating costs. Novel gas cleaning and conditioning technologies are undergoing development to reach this goal. Processes that operate at mild to high temperatures and incorporate multi-contaminant control to parts-per-billion levels are being explored. These include a two-stage process for hydrogen, Sulphur, trace metals, HCl, and particulates removal; membrane processes for control of H, S, Hg, and CO; and sorbents for NH control. Both ceramic and metallic filters are being assessed. Furthermore, investigation of technologies for mercury removal is currently underway. Promising technologies will be scaled-up and integrated into existing demonstration facilities.

Development of gas cleaning and conditioning technologies is a key element in achieving near-zero emissions while meeting system performance and cost goals. These technologies include advanced sorbents, reactor models, particulate filters, and other novel cleaning approaches, which remove gas contaminants.

When crude synthesis gas (syngas) leaves the gasifier, the gas stream must be cleaned and conditioned in order to remove feedstock contaminants. Not only must they be removed due to environmental concerns, but also to prevent downstream materials and equipment, such as chemical production catalysis or fuel cells, from being destroyed by contaminants. Immediately after leaving the gasifier, crude syngas is routed through heat exchangers and quench chambers to lower the temperature, then to a gas scrubber for further cooling and removal of solids such as slag. Many additional processes are used in combination to remove contaminants such as mercury and other heavy volatile metals, carbon dioxide, and Sulphur.

While gasification is already an ultra-clean technology, the cost of removing contaminants must be reduced. Many improvements are needed in gas cleaning and conditioning to overcome barriers to gasification system acceptance. Effective treatment of multiple contaminants is complicated and expensive, using numerous removal processes at varying temperatures.

Cleanup of contaminants must be more tightly integrated to increase efficiency and reduce cost. Gases that are formed by gasification will contain some or all of the contaminants listed (with their concomitant problems) in Table 4.2 (44).

Contaminant	Examples	Problems
Particulates	Ash, char, fluidized bed material	Erosion
Alkali metals	Sodium, potassium compounds	Hot erosion
Fuel-bound nitrogen	Mainly ammonia and HCN	NOx formation
Tars	Refractive aromatics	Clogs filters Difficult to burn, Deposits internally Corrosion
Sulphur, chlorine	HCl, H_2S	Corrosion, Emissions

Table 4.2 Gas contaminants with their problems

Contaminants	Clean-up method
Ash	Filtration, Scrubbing
Char	Filtration, Scrubbing
Inert	Filtration, Scrubbing
NH3	Scrubbing, SCR
HCl	Lime or Dolomite, Scrubbing, Absorption
SO2	Lime or Dolomite, Scrubbing, Absorption
Tar	Tar cracking, Tar removal
Na	Cooling, Condensation, Filtration, Adsorption
K	Cooling, Condensation, Filtration, Adsorption
Other metals	Cooling, Condensation, Filtration, Adsorption

Table 4.3 Main contaminants in gasification product gases and methods for removal.

The level of contamination depends mainly on two factors:

- ❖ The type of gasification process employed
- ❖ The type of feedstock used

If gas cleaning is not carried out, there will be erosion, corrosion and environmental problems in the downstream equipment. Table (4.3) gives a summary of the main contaminants in gasification product gases and methods for their removal.

4.1Tar removal Technologies

The main attempts to eliminate tar concentrate on three approaches:

4.1.1 Dry Technologies for Physical Removal of Tar

The raw gas leaves gasifiers at temperatures between 400 °C and 800°C. If hot gas filtration and tar cracking and/or reforming conversion follow, the temperature should be as high as possible. This is the case of physicochemical conversion of tar.

The use of dry, medium temperature technologies for the physical removal of tar is not yet envisaged. Fabric, ceramic, and metallic filters can remove near-dry condensing tar particles from gasifier gas. They are based on the principle that liquid tar condensing at a relatively high temperature will rapidly react to form solid species behaving as particulates rather than tar. The reasons they have not been used are the following; they will be only partially effective at temperature higher than 150°C; an important amount of tar will remain at the gas phase and pass through the filter without being retained. If a near liquid layer is formed on the surface of the filtering material, its stickiness will cause considerable mechanical problems and frequent failures. Both operating and capital costs seem very high.

4.1.2 Wet Technologies for Physical Removal of Tar

- Cooling towers and Venturi scrubbers: Cooling/scrubbing towers are usually used after cyclones as the first wet scrubbing units. All heavy tar components condense there. However, tar droplets and gas/liquid mists are entrained by the gas flow, thus rendering the tar removal rather inefficient. Venturi scrubbers are usually the next step. In Venturi scrubbers, typically 2 kWh/1,000 m^3 are consumed, corresponding to a pressure drop of approximately 7000 Pa.

- Demisters: Are centrifugal flow units designed to coalesce mist droplets from their gas flow. They resemble cyclones and hydro-cyclones and are usually used as a secondary stage in conjunction with classical wet scrubbing units. Their design depends on mist liquid phase properties and gas flow load. Tar and water are largely removed from producer gas at the exit of the second stage Venturi scrubber. Wastewater containing tar is settled out for insoluble tar skimming, then recycled back to the scrubbing loop.

- Granular filters: Granular filters can be used for cold and hot gas filtration. Inorganic beds, usually consisting of silica or alumina sand, are used as impact or surface filtration media. Static and mobile granular bed configurations have been used or are under development. When hot filtration is used, the filter operates usually at temperatures higher than 500°C so that only particulates are removed while tar remains at the gas phase. Sands are nonporous materials, characterized by low specific surface area. The most important development work in the field of hot gas filtration has been linked with coal gasification.

- Wet electrostatic precipitators: Electrostatic precipitators are widely used to remove fine solids and liquid droplets from gas streams. Although effectiveness with liquid droplets, they prove inefficient when tar is in the gaseous phase. This means that, when the target is the tar removal, high-temperature operation should be avoided. In such a case gas should be quenched before ESP use. The operation of an ESP is based on the passage of the gas stream through a high-voltage, negatively charged, area. Particles are thus charged and led to a collection area where opposite charge plates remove them from the stream. Very high, as well as very low, conductivities are detrimental to ESP operation. An appropriate balance is required for efficient operation. This means that the nature of tar can influence considerably the design of an ESP.

- E. Wastewater treatment: All wet gas cleaning systems generate wastewater that is contaminated with inorganic and organic pollutants. The concentration of the pollutants is always significant even for gasifiers with low tar production. Wastewater contaminants include dissolved organics, inorganic acids, NH_3, and metals. Regarding the dissolved organic compounds and most of the metal oxides, there are saturation points beyond which separation of phases occurs. Experimental data from runs with various feedstocks showed difference in organics concentration at equilibrium as a function of feedstock used.

Various technologies are proposed in the literature for these wastewater treatments before their final disposal. There is a short description of the available technologies that comprise extraction with organic solvent, distillation, adsorption on activated carbon, wet oxidation, and oxidation with hydrogen peroxide (H_2O_2), oxidation with ozone (O_3), incineration, and biological treatment. Recent works focused on wet oxidation and adsorption on mixtures of activated carbon and carbon-rich ashes produced during gasification. These techniques, together with biological treatment, seem to offer the best potential for eventual application at an Industrial / commercial level (149).

4.1.3 The Thermal, Steam, and Oxidative Conversion of Tars

- Thermal Destruction: The consensus seems to be that temperatures in excess of 1000°C, at reasonable residence times, are necessary to destroy the refractory unsubstituted aromatics, without a catalyst. Apart from the economics and materials problems, such thermal decomposition can produce soot that can be even more troublesome than the aromatics for some processes. Benzene seems to be the least reactive, thermally, of the light aromatics.

- Steam Reforming or Cracking: Tars produced in air gasification are more refractory than those produced in steam. Tars produced in the gasification of biomass with steam are different than those produced in spruce gasification of biomass in air or with steam + O_2. Tar yields decrease with increasing gasification temperature and with steam / biomass ratio. It is postulated that steam gasification tars have more phenolics and C-O-C bonds, which are easier to reform. Pure steam produces a more phenolic tar, which is easier to catalytically convert than tar from steam + O_2 gasification. In the partial oxidation of pyrolysis vapors, the addition of steam tends to enhance the formation of benzene and toluene. Steam also enhances phenol formation. Steam reduces the concentration of oxygenates in a fluid-bed gasifier.

- Partial Oxidation: Oxygen or air added to steam seems to produce more refractory tars but at lower levels, while enhancing the conversion of primaries. When oxygen is added selectively to different stages, such as in secondary zones of a pyrolysis-cracker reactor, tars can be preferentially oxidized.

4.1.4 The Catalytic Destruction of Tars

- Nonmetallic Oxides: Calcined dolomites have been extensively investigated as biomass gasifier tar destruction catalysts. These naturally occurring catalysts are relatively inexpensive and disposable so it is possible to use as primary catalysts (in bed) as well as in secondary, downstream reactors.

Dolomite is a calcium magnesium ore with the general chemical formula CaMg $(CO_3)_2$ that contains ~20% MgO, ~30% CaO, and ~45% CO_2 on a weight basis, with other minor mineral impurities. Dolomites, in their naturally occurring form, are not nearly as active for tar conversion until they are calcined. Calcination of dolomite involves decomposition of the carbonate mineral, eliminating CO_2 to form MgO - CaO.

Complete dolomite calcination occurs at fairly high temperatures and is usually performed at 800ºC - 900ºC. The calcination temperature of dolomite, therefore, restricts the effective use of this catalyst to these relatively high temperatures. Calcined dolomite also loses its tar conversion activity under conditions where the CO_2 partial pressure is greater than the equilibrium decomposition pressure of dolomite. This becomes an important issue in pressurized gasification processes. As the pressure of the process increases, the operating temperature of calcined dolomite reactor must be increased to maintain catalyst activity. Calcination also reduces the surface area of the dolomite catalyst and makes it more friable. Severe catalyst attrition and the production of fine particulate material plague the use of calcined dolomite in fluidized bed reactors.

- Commercial Nickel Reforming Catalysts: A wide variety of Ni-based steam reforming catalysts are commercially available because of their application in the petrochemical industry for naphtha reforming and methane reforming to make syngas. Nickel-based catalysts have also proven to be very effective for hot conditioning of biomass gasification product gases. They have high activity for tar destruction, methane in the gasification product gas is reformed, and they have some water-gas shift activity to adjust the $H_{2:}$ CO ratio of the product gas. The content of H_2 and CO of the product gas increases, while hydrocarbons and methane are eliminated or substantially reduced for catalyst operating temperatures above ~740ºC. Some studies have also shown that nickel catalyzes the reverse ammonia reaction, thus reducing the amount of NH_3 in gasification product gas.

Commercial Ni steam reforming catalysts have also been widely used for biomass gasification tar conversion. They have high, demonstrated activity for tar destruction with the added advantages of completely reforming methane and water-gas shift activity that allows the H_2: CO ratio of the product gas to be adjusted. Some studies have also shown that nickel catalyzes the reverse ammonia reaction thus reducing the amount of NH_3 in gasification product gas (149).

4.1.5 Adsorption of Tars by Carbon materials

The most recent research activities found the carbon materials are very effective and practical method for tar cracking during biomass gasification; these materials include Active carbon, Char coal and Black coke. The theory of adsorption will be described in the following chapter and a detailed description of the utility of carbon materials as a bed filter in tar removal through biomass gasification process is in chapter (8).

5. Fundamentals and theory of Adsorption

Adsorption is the term for the enrichment of gaseous or dissolved substances (the adsorbate) on the boundary surface of a solid (the adsorbent). On their surfaces adsorbents have what we call active centers where the binding forces between the individual atoms of the solid structure are not completely saturated (Fig.5.1). At these active centers an adsorption of foreign molecules takes place. The adsorption process generally is of an exothermal nature. With increasing temperature and decreasing adsorbate concentration the adsorption capacity decreases. For the design of adsorption processes it is important to know the adsorption capacity at constant temperature in relation to the adsorbate concentration.

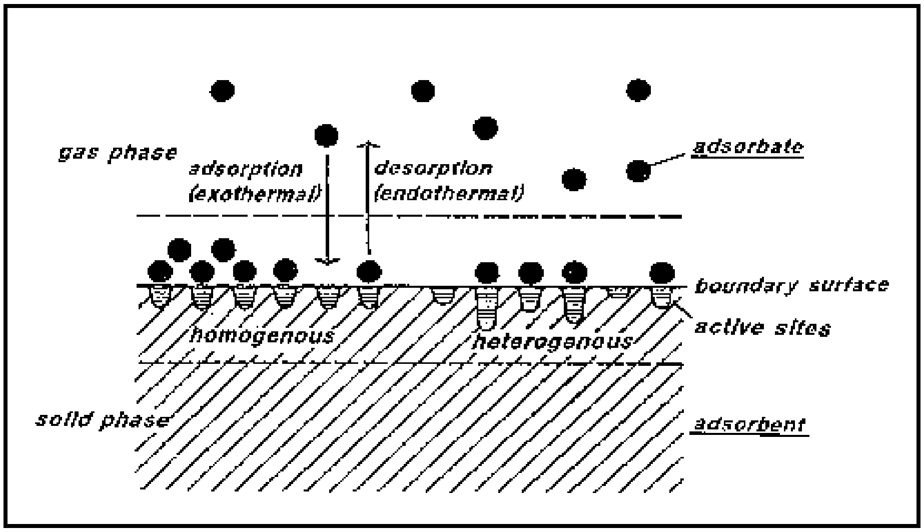


Figure 5.1 Fundamentals of adsorption and desorption

Adsorption is the process by which particles, e.g., solvent molecules, become attached from a fluid phase to the surface of a solid adsorbing material. Adsorption is a reversible process. The process always releases heat.

5.1 Adsorption of particles from a gas to a solid surface

The adsorbate - the adsorption substance to which molecules is attached - is in a state of equilibrium with the fluid phase, i.e., gas or liquid. The more the adsorbing material is loaded, the higher is its vapor pressure, very low loads whose equilibrium concentration is in the range of the statutory emission limit represent a single-place adsorption. In this range, the vapor pressure of the adsorption substance is proportional to the load, which formally corresponds to Henry's law. If pore condensation occurs, the vapor pressure of the adsorption substance enters the range of the vapor pressure of the liquid phase (161).

How much substance can be taken up by the adsorbing substance, depends on three factors:

- Temperature: Higher temperatures reduce the load because the adsorption process releases heat. Therefore, it is possible to release the adsorbed material from the adsorbing material and thereby regenerate it by increasing the temperature.

- Chemical interaction: The properties of the adsorbing material and the adsorbed substance, most of all the polarity, determine the degree of interaction between both.
- Partial pressure: The higher the concentration of the adsorbed material in the gaseous phase the more material is adsorbed. Reversely, if the concentration of the adsorbed material is low in the gaseous phase, some adsorbed material is released from the adsorbing surface. This means that the adsorbing material can be regenerated with pure gas. The mathematical presentation of this context is referred to as adsorption isotherm.

The adsorption isotherm does not describe time-related factors because it reflects an equilibrium state. It is generated - often for the single grain - by determining the amount of molecules attaching to the adsorbing material after hours of establishing the equilibrium in a static gas atmosphere. In the technical adsorber, the gas molecule is exposed to the adsorbing material only for a few seconds. Diffusivity, another factor critical to the function of the adsorber, comes into play here. Diffusivity is composed of four sub-components relating to the steps of the adsorption process:

- Diffusion of the particle through the gaseous phase, i.e., the empty space of the adsorber;
- Diffusion through the boundary layer into the pore,
- Diffusion along the surface of the adsorbing material, and,
- Diffusion through the solid substance.

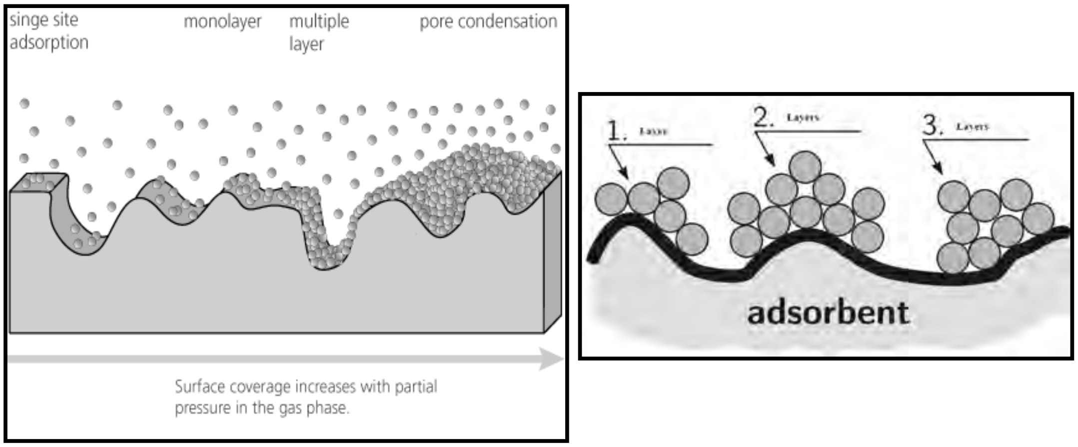


Figure 5.2 Adsorption process

5.2 Adsorption Parameters of Activated Carbon

Adsorption is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. The force acts in a similar way to gravitational forces between planets. London Dispersion Forces are extremely short ranged and therefore sensitive to the distance between the carbon surface and the adsorbate molecule, they are additive, meaning the adsorption force is the sum of all interactions between all the atoms. The short range and additive nature of these forces results in activated carbon having the strongest physical adsorption forces of any material known to mankind.

- Gas Phase Adsorption - This is a condensation process where the adsorption forces condense the molecules from the bulk phase within the pores of the activated carbon. The driving force for adsorption is the ratio of the partial pressure and the vapour pressure of the compound.
- Liquid Phase Adsorption - The molecules go from the bulk phase to being adsorbed in the pores in a semi-liquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound.

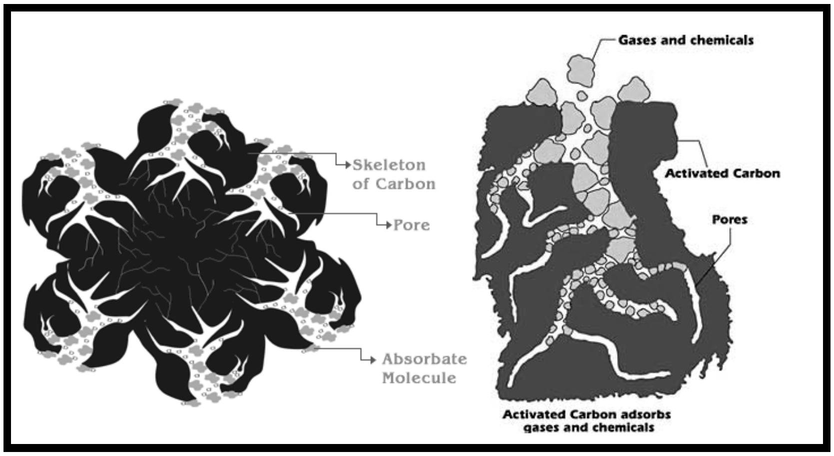


Figure 5.3 Active carbon particles structure

The pore space is the internal volume of the carbon granule. It consists of all the cracks and crevices created when the coal is crushed and glued back together, and the volume between the graphite plates.
The distance between the graphite plates determines whether the space is an adsorption pore or a transport pore.

Adsorption pores are the internal volume where the graphitic plates are very close together creating a higher energy. Higher energy is important to adsorption because it is the energy that "holds" the contaminant (the carbon "adsorbs" the contaminant). The volume where the graphite plates are far apart and the cracks and crevices make up the transport pores. It is important to note that all adsorption takes place in the adsorption pores and not the transport pores (162).
There is a natural attractive force between all things in the universe. Gravity is one of these forces. In adsorption theory, the force between contaminate and the carbon is the adsorptive force. It technically is a Van der Waals force. It is this attractive force that enables adsorption to occur. The forces are a function of the distance between the two objects. The closer together the objects are, the higher the attractive force is. The higher the attractive force, the higher the "energy" level.

Transport pores are the internal volume of the carbon granule where the graphitic plates are far apart or the cracks and crevices of the particle. The transport pore act as the "highways" for the contaminants to reach the adsorption pores where they are adsorbed. It is important to note that no adsorption takes place in the transport pores. Transport pores are vitally important, as they allow access to the adsorption pores - especially those deeper within the carbon granule.

Once the contaminant enters the carbon granule via the transport pore space, it diffuses into the carbon matrix until it enters the smaller pores where the adsorptive forces begin to take effect, once it reaches a higher-energy area, it can no longer migrate (or diffuse) because the adsorptive force is stronger than the diffusion force. The contaminant is adsorbed to the carbon surface by the adsorptive forces (the Van der Waals forces). In this state, the contaminant is referred to as the adsorbate (164).

5.3 Types of Adsorption

Adsorption usually classified into two types as following:

- Physical Adsorption or Physisorption

When the force of attraction existing between adsorbate and adsorbent are weak Van der Waals forces of attraction, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e.:

$\Delta H_{adsorption}$ is 20 - 40KJ/mol.

It takes place at low temperature below boiling point of adsorbate. As the temperature increases in, process of physisorption decreases.

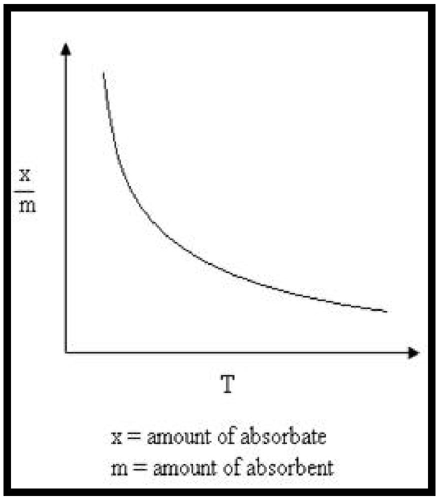


Figure 5.4 Physical Adsorption vs. Temperature graph

- Chemical Adsorption or Chemisorption

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption i.e.:

$\Delta H_{adsorption}$ is 200 - 400 KJ/mol

It can take place at all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

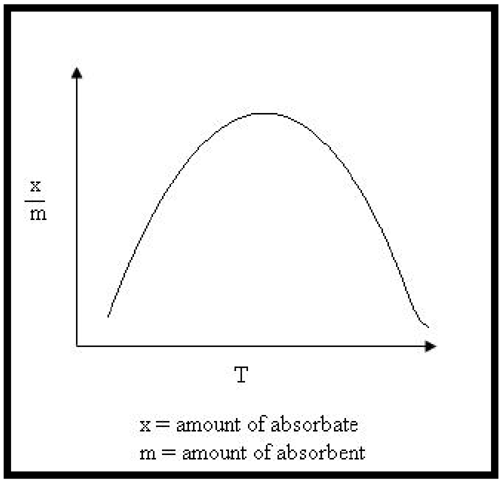


Figure 5.5 Chemical Adsorption vs. Temperature Graph

5.4 Adsorption Isotherm

The process of Adsorption is usually studied through graphs called as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature.

In the process of adsorption, adsorbate gets adsorbed on adsorbent.

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$

According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.

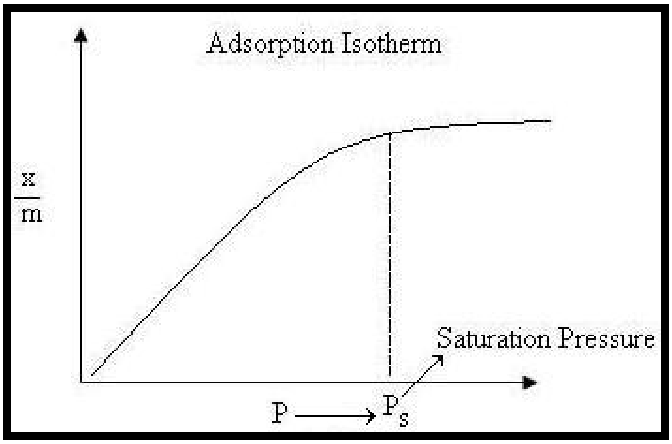


Figure 5.6 Basic Adsorption Isotherm

From the graph, we can predict that after saturation pressure Ps, adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure (163).

- Freundlich Adsorption Isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$$x/m = kP^{1/n}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

- Langmuir Adsorption Isotherm

In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. The Langmuir equation is typically used to describe adsorption of gas in coal and takes the form:

$$P/V = 1/BV_m + P / V_m$$

Where P is the equilibrium pressure, V is the volume of gas adsorbed at equilibrium, Vm, is the volume of adsorbate occupying a monolayer, and B is an empirical constant. The Langmuir Isotherm can be written as:

$$V\ (P) = V_L\ P\ /\ (P_L + P)$$

P = gas pressure
V (P) = predicated amount of gas adsorbed at P
V_L = Langmuir volume parameter: the maximum volume of gas adsorbed as gas pressure approaches infinity
P_L = Langmuir pressure parameter: the pressure at which the volume of sorbed gas is 50% of the maximum value.

This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where A (g) is unadsorbed gaseous molecule, B(S) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

One of the basic assumptions of Langmuir Adsorption Isotherm was that adsorption is monolayer in nature. Langmuir adsorption equation is applicable under the conditions of low pressure. Under these conditions, gaseous molecules would possess high thermal energy and high escape velocity. As a result of this less number of gaseous molecules would be available near the surface of adsorbent.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

θ = *Number of occupied adsorption sites / Total number of possible sites*

$$\theta = KP\ /\ 1+KP$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase .The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only (162).

At lower pressure, KP is so small, that factor ($1+KP$) in denominator can almost be ignored. So Langmuir equation reduces to:

$$\theta = KP$$

At high pressure *KP* is so large, that factor (*1+KP*) in denominator is nearly equal to *KP*. So Langmuir equation reduces to:

$$\theta = KP/KP = 1$$

Or:

$$\theta = cz / (1 - z) \{1 - (1 - c) z\}$$

And:

$$z = \frac{P}{P*}$$

In this expression P^* is the saturation pressure of the gas (i.e., the vapor pressure of the liquid at that temperature), and *c* is a constant:

$$c = \exp \{\Delta_{des} H - \Delta_{vap} H) / RT\}$$

- BET adsorption Isotherm

BET theory is a rule for the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. BET Theory put forward by Brunauer, Emmett and Teller explained that multilayer formation is the true picture of physical Adsorption.

Under the condition of high pressure and low temperature, thermal energy of gaseous molecules decreases and more gaseous molecules would be available per unit surface area, due to this multilayer adsorption would occur. The multilayer formation was explained by BET Theory and the BET equation is given as:

$$V_{total} = V_{mono}\, C\, [P/P_O] / [1-P/P_O]\ [1+C\, (P/P_O) - P/P_O]$$

Another form of BET equation is:

$$P/ V_{total}\, (P-P_O) = 1/ V_{mono}\, C + (c-1)/V_{mono}\, C\, [P/P_O]$$

Where V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules,

$$K_1/K_L$$

Here $\Delta_{des}H$ and $\Delta_{vap}H$ are the enthalpies of desorption from the monolayer and of vaporization of the liquid adsorbate, respectively

The ratio is designated *C*. K_1 is the equilibrium constant when single molecule adsorbed per vacant site and K_L is the equilibrium constant to the saturated vapor liquid equilibrium.

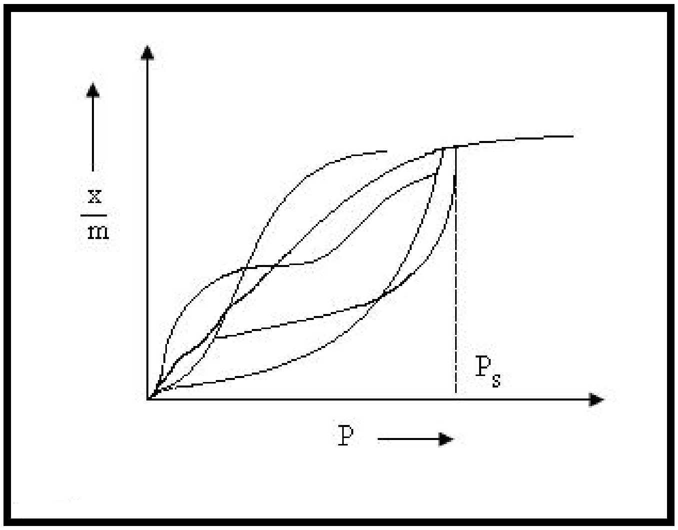


Figure 5.7 Five different types of adsorption isotherm

The BET isotherm is found to describe adequately the Physisorption at intermediate coverage (θ = 0.8 - 2.0) but fails to represent observations at low or high coverage. The BET isotherm is reasonably valid around θ =1.0, however, and this is useful in characterizing the area of the absorbent. If one can determine experimentally the number of moles of adsorbate required to give θ = 1.0 (i.e. a monolayer), one can determine the specific area of the absorbent:

$$\bar{A} = \text{surface area of absorbent } [m_2] \,/\, \text{mass of absorbent } [g]$$

6. Biomass gasification kinetics

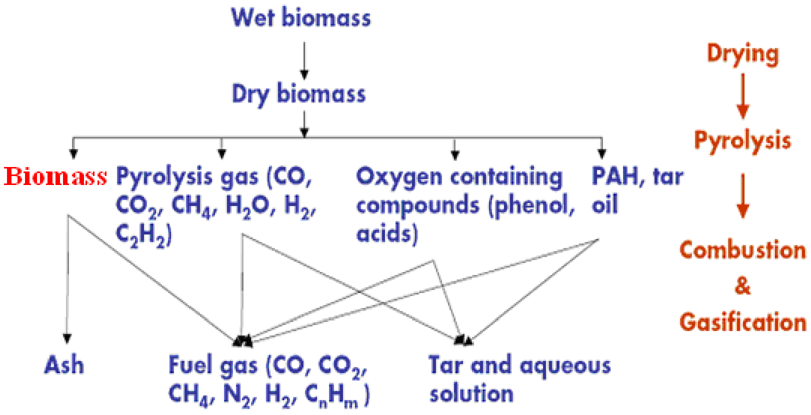


Figure 6.1 Different stages of biomass Pyrolysis

A correct design of the reactor is fundamental to achieve an optimal conversion of the chemical energy present into the biomass feedstock. To evaluate syngas composition, the main steps of the calculation procedures are summarized as follows:

- Input of the biomass composition and the oxidization type.
- Input of the general reactor design parameters: length, thickness and wall materials.
- Evaluation of the bottom temperature.

- ❖ Studying of bed hydrodynamics, heat and mass transfer and gasification kinetics.
- ❖ Comparison of the results with experimental data.

6.1 Evaluation of the overall reaction kinetics

The gasification reactions occur at equilibrium and thermodynamic equilibrium compositions are predicted for biomass. The pyrolysis and partial combustion are supposed to be much faster than the gasification, and then the related solid (carbon) and volatile products (CO_2, CH_4, and H_2O) are fixed as the initial gasification species. Their amount depends on type of biomass considered. The only hydrocarbon accounted in the syngas has been CH_4, while the other minor species C_nH_m have been neglected and eventually included in the CH_4. The amount of H_2, CO, CO_2, CH_4 and Char in molar fraction per mole of biomass has been evaluated.

6.2 Equilibrium of Biomass Gasification

The main aim is to produce producer gas from biomass and to be used for power generation; the tar in the outlet gases is cracked thermally in the tar cracking unit (The carbon filter).

6.2.1 Assumptions

1. Biomass is represented by the general formula $CH_x\,O_y$.
2. The gasification products contain CO_2, CO, H_2, CH_4, N_2, H_2O and un-burnt carbon.
3. The reactions are at thermodynamic equilibrium.
4. The reactions proceed adiabatically.

Based on the above assumptions, the general reaction of biomass with air and steam is written as:

$$CH_x\,O_y + z\,(p\,O2 + (1-p)\,N_2) + k\,H_2O = a\,CO_2 + b\,CO + c\,H_2 + d\,CH_4 + e\,N_2 + f\,H_2O + g\,C \qquad (1)$$

Where, x and y are the H/C and O/C mole ratio, respectively. The moisture content of the biomass is neglected and the product quality depends on the x and y. The above reaction represents an overall reaction of a number of competing intermediate reactions take place during the process, these are:

1) Oxidation: $C + O_2 = CO_2$ (2)
2) Steam gasification: $C + H_2O = CO + H_2$ (3)
3) Boudouard reaction: $C + CO_2 = 2CO$ (4)
4) Methanation reaction: $C + 2H_2 = CH_4$ (5)
5) Water gas-shift reaction: $CO + H_2O = CO_2 + H_2$ (6)

Out of these only four reactions are independent reactions, which are chosen as oxidation, steam gasification, Boudouard reaction, and the methanation reaction. The water gas shift reaction can be considered as the subtraction of the steam gasification and Boudouard reactions. Oxidation reaction is typically assumed to be very fast and goes to completion and the three reactions namely Boudouard reaction, steam gasification and methanation are in equilibrium (76). The three equilibrium relations for the three reactions (other than oxidation) are:

1) Boudouard reaction:

$Ke1 = Y^2 \mathrm{co}\, \mathrm{P}t / Y co_2$ (7)

2) Steam gasification reaction:

$Ke2 = Y \mathrm{co}\, YH_2\, \mathrm{P}t / YH_2O$ (8)

3) Methanation reaction

$Ke3 = YCH_4 / Y^2 H_2\, \mathrm{P}t$ (9)

The equilibrium constants are given by

$In\ Ke = -\Delta G_0 / RT$ (10)

Where, ΔG_0 is the Gibb’s free energy (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant in consistent units (84). The energy balance can be considered as follows the heat of the overall gasification reaction (1) is given by:

$$\Delta H_R\,(T) = \Delta H_R\,(T_R) + \sum_{i-1}^{n} n_i \int_{T_R}^{T} C\, d\, T \qquad (11)$$

Heat of reaction at the reference temperature is calculated using specific heats of combustions of the species.

$$\Delta H_R\,(T_R) = \Delta H_{C\ Biomass} - \Delta H_{C\ CO} - \Delta H_{C\ H2} - \Delta H_{C\ CH4} \qquad (12)$$

Thus:

$$0 = \Delta H_R\,(T_R) + \sum_{i=1}^{n} n_i \int_{TR}^{T} C\, dT \qquad (13)$$

Where:

ΔH_R = The heat of reaction

ΔH_C = the heat of combustion of species

n_i = The moles of species

Cpi = The specific heat capacity of species.

The eight non-linear algebraic equations (7-13 and 14) are solved simultaneously in order to determine a, b, c, d, e, f, g (which determine the product gas composition) and the adiabatic temperature, at various pressures without energy balance. This gives the expected exit gas compositions at each temperature and pressure (47).

7. Research Activities and Work Objectives

7.1 Experimental Facilities

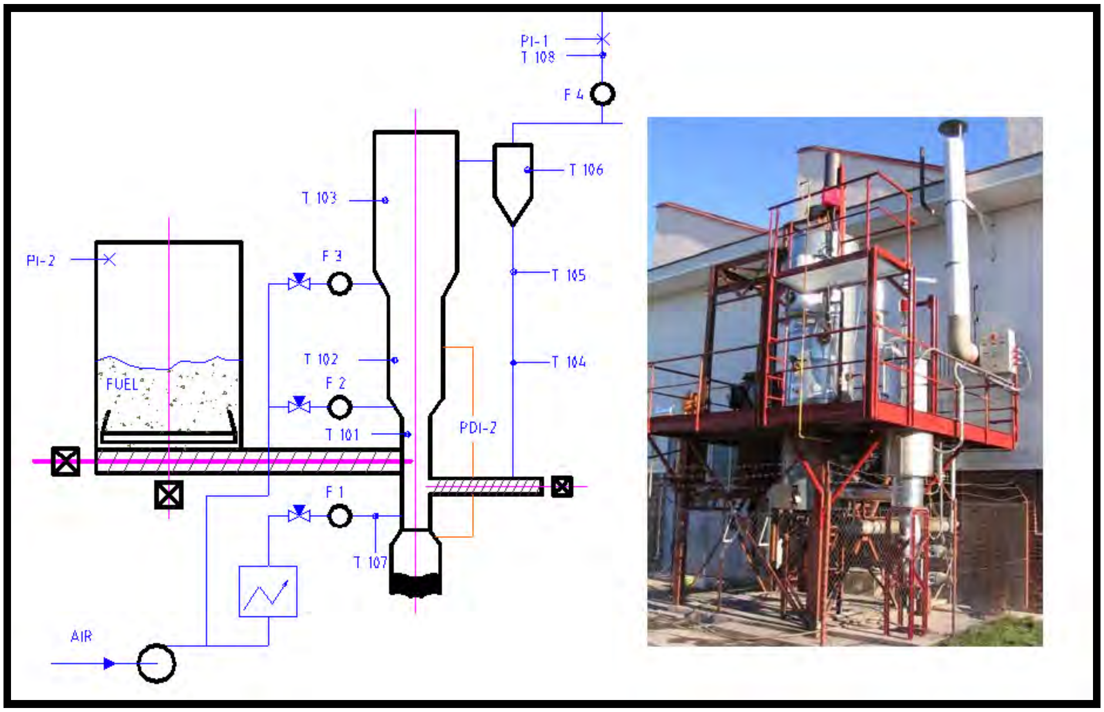
This section will describe relevant details of the experimental techniques and the procedures involved in this work. All the experimental works carried out within the Institute of Power Engineering, Department of Mechanical Engineering at Brno University of Technology, Czech Republic.

Experiments will be carried out at fluidized bed atmospheric gasifier with stationary fluidized bed called Biofluid 100 (Fig.7.1). The unit can be operated in both gasifying and combustion modes. Fluidized bed gasifier start-up to steady state is carried out by way of combustion mode. Process temperature control is carried out by changing the fuel to air ratio with temperature control range being within the 750°C to 900 °C brackets. Average heating value of the produced gas ranges from 4 MJ/m³n to 7 MJ/m³n, the content of solid particles is in the region 1.5 g/m^3_n to 3 g/m^3_n and the content of tars from 1 g/m³n - 5 g/m³n depending on fuel used and operating conditions.

Fuel comes from rake-equipped storage tank to be fed to the gasifier in batches by a screw feeder. Blower-compressed air is delivered to the gasifier, to under its grate, as primary air ensuring partial oxidization of fuel and maintaining the fluidized bed. Moreover, air can be supplied at two other levels as secondary air and tertiary air. In a cyclone, the produced gas is rid of particulates and consequently combusted by a burner equipped with a small stabilizing natural gas fired burner with its own air inlet. Ash from the gasifier is discharged to ash bin on intermittent basis by means of a purpose-designed special moving grate. To be able to examine impact of air preheating, electric heater has been installed at the back of the blower.
Simplified diagram of the experimental facility is shown in (Fig.7.1) more detailed description is given in (Fig.7.2). The parameters of the gasifier are as follows:

- Output (in generated gas) 100 kW*t*
- Input (in fuel) 150 kW*t*
- Fuel consumption max. 40 kg/h
- Air flow max. 50 m^3_n /h

The type of fuel to be used is limited, primarily, by the size of the fuel screw feeder and then by moisture content. Optimum moisture content is from 20% to 30%. Wood biomass mostly consists of shavings or small wood chips, their size being 2 cm to 3 cm, herbaceous biomass either mostly consists of finely chopped matter or smaller size pellets. Chopped matter did not prove to be much of a success as there are major problems with fuel feeding, particularly with crust formation in the fuel storage bin. Neither is this type of fuel treatment optimal for formation of fluidized bed



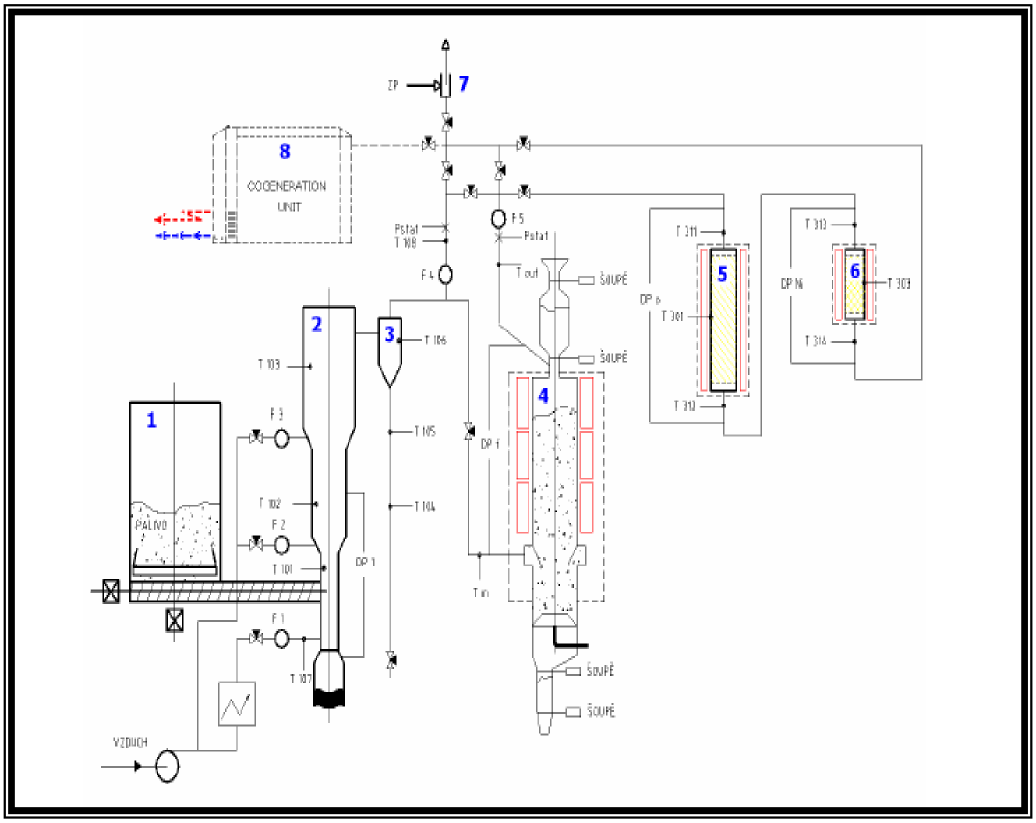
T101-103: temperatures in the gasifier, T106: temperature inside the cyclone, T107: temperature of the incoming primary air, T108: gas temperature at jacket outlet, F 1-3: air flows, F4: gas flow, P stat: outlet gas pressure, Pstat1: tank pressure, DP1: fluidized bed pressure difference

Figure 7.1 (A) and (B) Simplified layout of atmospheric fluidized Biofuel bed gasifier Connections

7.2 Experimental unit Biofluid 100

Gas quality measurement is usually carried out in two ways. One consists of an on-line monitoring of gas composition with simultaneous gas sampling to gas-tight glass sample containers. The samples are subsequently analyzed using gas chromatograph. Tar sampling is carried out in line with IEA methodology by capturing tar in a solution that is subsequently analyzed by gas chromatograph with mass spectrometer. Presences of HCl, HF and NH_3 in the gas are examined by their trapping in an (NaOH) solution.

Operating parameters are monitored during operation and continuously recorded by the control computer. They include, in particular, mass flow of fuel, temperatures at various points of the unit, pressure difference in the fluidized bed, gas flow and pressure, and the temperature and flow of primary air. The layout of a complete cleaning line was designed with an optional configuration of connection. The fuel is brought to the fuel storage (1), from where it is fed by screw feeder to the gasifier (2). The generated gas passes cyclone to remove semi-coke (3). The cyclone is followed by gas cleaning line consisting of hot catalytic filter (4), and the filter filled with the carbon material (6). At present, the gas is combusted using flame holder (7), the final step will consist of connection of a CHP unit and a combustion engine (8).



1. Fuel storage 2. Gasifier 3. Cyclone 4. HCF
6. Carbon filter 7. Burner 8. Combustion engine

Figure.7.2 Overall layout of Biofluid 100

7.3 Objective and outline of the research

The scientific objectives of this project concern the set up and test of the gas cleaning system adapted to biomass gasification plant and to demonstrate the concept of a biomass air gasification process to produce fuel gas having a higher heating value with less tar formation by the utilization of different carbon materials as a bed filter . The experiments will investigate the impacts of parameters variation such as temperature profiles in the reactor, pressure distribution and the air/biomass ratio on tar formation, gas composition and energy transformation including carbon conversion and cold gas efficiency. Additional objectives of the research are:

- contribute to the knowledge about biomass and solid waste pyrolysis and gasification;
- optimize the biomass gasification process in order to improve the syngas quality and to obtain high energy efficiencies;
- To develop and evaluate gas cleanup and conditioning systems, including tar and hot gas particulate removal, required for the production of fuels and chemicals from syngas derived from biomass gasification.
- Compare traditional and alternative energy production of biomass and assessment of energy and environmental balance.

The research is based on an extensive literature search will mainly focus on the following:

- Processes of gasification of various kinds of wood biomass
- Primary methods of tar removal
- Secondary methods of tar removal, using the activated carbon, char coal and black coke as the bed main filter with the help of utilization of the dolomite as a hot catalytic filter (HCF) which traps dust particles contained in the produced gas.

The carbon filter mainly serves for removal of tar that is the biggest problem in subsequent energy use of the gas.

Tar formation is one of the major problems to deal with during biomass gasification. Tar condenses at reduced temperature, thus blocking and fouling process equipments such as engines and turbines. Considerable efforts have been directed on tar removal from fuel gas. Tar removal technologies can be divided into two approaches; hot gas cleaning after the gasifier (secondary methods), and treatments inside the gasifier (primary methods). Although secondary methods are proven to be effective, treatments inside the gasifier are gaining much attention as these may eliminate the need for downstream cleanup. In primary treatment, the gasifier is optimized to produce a fuel gas with minimum tar concentration. The different approaches of primary treatment are:

- Proper selection of operating parameters.
- Use of bed additive/catalyst.
- Gasifier modifications.

The operating parameters such as temperature, gasifying agent, equivalence ratio, residence time, etc. play an important role in formation and decomposition of tar.

There is a potential of using some active bed additives such as dolomite, olivine, char, etc. inside the gasifier.

Different carbon materials are experimented to be very effective not only for tar reduction, but also for decreasing the amount of tar compounds. The reactor modification can improve the quality of the product gas. The concepts of two-stage gasification and secondary air injection in the gasifier are of prime importance.

8. Experimental work procedure

8 .1 Testing materials

Three different kinds of carbon materials have been chosen, char coal, active carbon and black coke. A detailed explanation of the testing procedure will be shown in following chapter.

8.1.1 Active carbon

Activated carbons are complex products, solid, porous, black carbonaceous material, tasteless (Budavari, 1996). Activated carbon is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface which are difficult to classify on the basis of their behavior, surface characteristics and preparation methods. However, some classification is made for general purpose based on their physical characteristics.

A gram of activated carbon can have a surface area in excess of 500 m², with 1500 m² being readily achievable with average pore diameter ranges from 20 to 40 microns, typical for most commercially used adsorbents. Adsorption capacity of the activated carbon depends on:

- Physical and chemical characteristics of the adsorbent (carbon);
- Physical and chemical characteristics of the adsorbate;
- Concentration of the adsorbate in liquid solution;
- Characteristics of the liquid phase (e.g. pH, temperature)
- Amount of time the adsorbate is in contact with the adsorbent (residence time).

In industrial operations, adsorption is accomplished primarily on the surface of internal passage within small porous particles. Three basic mass transfer processes occur in series:

- Mass transfer from the bulk gas to the particle surface.
- Diffusion through the passages within the particle surface.
- Adsorption on the internal particle surfaces.

Each of the process depends on the system operating conditions, the physical and chemical characteristic of the gas steam and the solid adsorbent. Often one of the transfer processes will be significantly slower than the other two and will control the overall transfer rate, the other two will operate nearly at equilibrium. Heat transfer may also play an important role in an adsorption system. The adsorption process is exothermic.

Activated carbon does not bind well to certain chemicals, including alcohols, glycols, ammonia, strong acids and bases, metals and most inorganic, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid. Activated carbon does adsorb iodine very well and in fact the iodine number is used as an indication of total surface area

Activated carbon can be used as a substrate for the application of various chemicals to improve the adsorptive capacity for some inorganic (and problematic organic) compounds such as hydrogen sulfide (H_2S), ammonia (NH_3), formaldehyde (HCOH), radioisotopes iodine-131 (^{131}I) and mercury (Hg). This property is known as chemisorptions. There are many types of activated carbon products each is used for a different application such as:

- Powdered activated carbon (PAC)
- Granular activated carbon (GAC)
- Extruded activated carbon (EAC)
- Impregnated carbon
- Polymers coated carbon

Figure 8.1 Types of the Industrial Active Carbon

Industry	Application
General Gas Application	Filters for gas removal, Purification of various raw - material and process gases.
Solvent Recovery and catalyst	Removal of generally harmful and odorous gases, Recovery of solvents.
Water Purification	Water Dechlorination.
Liquid Phase Refining	De-coloration and refining of raw material and intermediates.
Liquid Phase De-coloration	Decolonization in Food processing industry, Cleaning solvents and waste water.

Table 8.1 Active carbon industrial applications

The activated carbon used in all the experiments was manufactured by **(Resorbent s.r.o)**. Reactivation of saturated activated carbon is done in the rotating countercurrent furnace with active medium (hot gases and water vapour) with gradual growth of temperature to 820 - 850 °C and with the period of delay - 30 minutes. The specification discription of the activated carbon used is shown below:

Description	Coal based activated carbon produced by high temperature steam activation
Particle size (ASTM D2862)	min. 95% no bigger particles 200 MESH)
Iodine number (ASTM D4607)	> 900 mg/g min.
Surface area (BET N_2)	> 900 m²/g min.
Ash (ASTM D2866)	< 15% max.
Moisture (ASTM D2867)	5% max.

Table 8.2 Active Carbon MA C5 P200 properties (134)

8.1. 2 Char coal

The characteristics of charcoal products vary widely from product to product. Thus it is a common misconception to stereotype any kind of charcoal, which burns hotter. There are different types of Charcoal:

- Lump charcoal
- Briquettes
- Extruded charcoal

Charcoal usually used for:

- Cooking fuel
- Industrial fuel
- Automotive fuel
- Purification / Filtration
- Art

8.1.3 Black coke:

Discovered by accident to have superior heat shielding properties when combined with other materials, coke was one of the materials used in the heat shielding on NASA's Apollo program space vehicles. In its final form, this material was called AVCOAT 5026-39. This material has been used most recently as the heat shielding on the Mars Pathfinder vehicle. Although not used for modern day space shuttles, NASA is utilizing coke and other materials for a new heat shield for its next generation space craft, named Orion, which is due to be completed in 2014 (31). Coke is used as a fuel and as a reducing agent in smelting iron ore in a blast furnace. Since smoke-producing constituents are driven off during the coking of coal, coke forms a desirable fuel for stoves and furnaces in which conditions are not suitable for the complete burning of bituminous coal itself. Coke may be burned with little or no smoke under combustion conditions, while bituminous coal would produce much smoke. Coke may be used to make fuel gases; these useful gases require careful handling because of the risk of carbon monoxide poisoning.

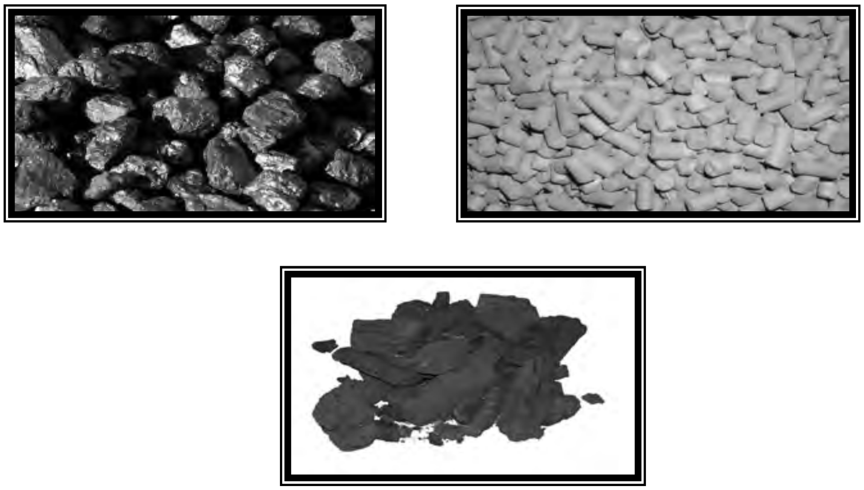


Figure 8.2 Materials Used in the Experiments

8.2 Fuel used and Properties

Wood chips were used as a feedstock during the experiments to achieve the higher fuel use efficiency; the two key quality aspects for wood chips are moisture control and particle size. A uniform particle size is very important for reliable operation of chip feed and burning mechanism. A load of wood chips fuel should have no stones or soil, little dust, and crucially, no oversize chips, twigs or long slivers – these can jam feed mechanism. In principle, less than 30% of moisture content would be ideal.

Both the results of proximate and ultimate analyses show that woody plants make better quality fuels. There is no substantial difference between individual fuels in the two major categories (Culm plants and Woody plants). Woody plants, however, in general, contain higher amounts of combustible matter, particularly volatile matter, which is important for gasification, and smaller amounts of ash matter. Fig.8.3 show the wood chips used in the experiments.

Figure 8.3 Wood Chips Used

As shown by ultimate analyses, woody plants contain larger amounts of carbon and smaller amounts of nitrogen (14).

	Woody biomass	Agricultural biomass	other waste
Typical biomass fuel	wood chips, forest residue, paper mill waste	Willow, straw, alfalfa	Sewage sludge
Ash content	1 - 5 % w	4 - 11% w	10 - 45% w
Sulphur content	< 0.1 % w	0.1 - 0.3 % w	0.1 - 1 % w
Nitrogen content	0.4 - 0.7 % w	0.5 - 3.0 % w	0.5 - 6% w
Chlorine content	< 0.1 %w	0.1 - 0.25%w	0.1 - 1%w
Alkaline (Na+K)	0.05 - 0.4%w	0.3-3 %w	n/a

Table 8.3 Properties for woody plants (147)

8.3 Testing Procedure

In order to prepare the Char coal and the Black coke, first of all it was necessary to go through the following operations:

- The grinding

A hammer was used to grind the multiple size pieces of raw materials, smaller sizes are more convenient for testing procedure and for it is impossible to get all the pieces in the certain size required, this operation should be followed by filtration.

- The Filtration

The equipment (ANALYSETTE 3.PRO) was used for filtration, only the 2 mm particles size were collected where the slaving time was 4 minutes.

- The weighing

400 ml, 200ml of each of the testing materials have been chosen for filter filling separately for each series of experiments. A sensitive scale was used to certify the amount of the carbon material weight 100g and 50g.

Figure 8.4 (ANALYSETTE 3.PRO) and the Carbon material after filtration

Figure 8.5 Testing flask

- Filter filling

The filter was filled with the mentioned amount of the carbon materials, 400ml; 100g of each material was used in the first series of experiments then the amount of 200 ml,50g of each material has been used in the second and third serious of experiments. . Fig.8.6 shows the filter filling procedure:

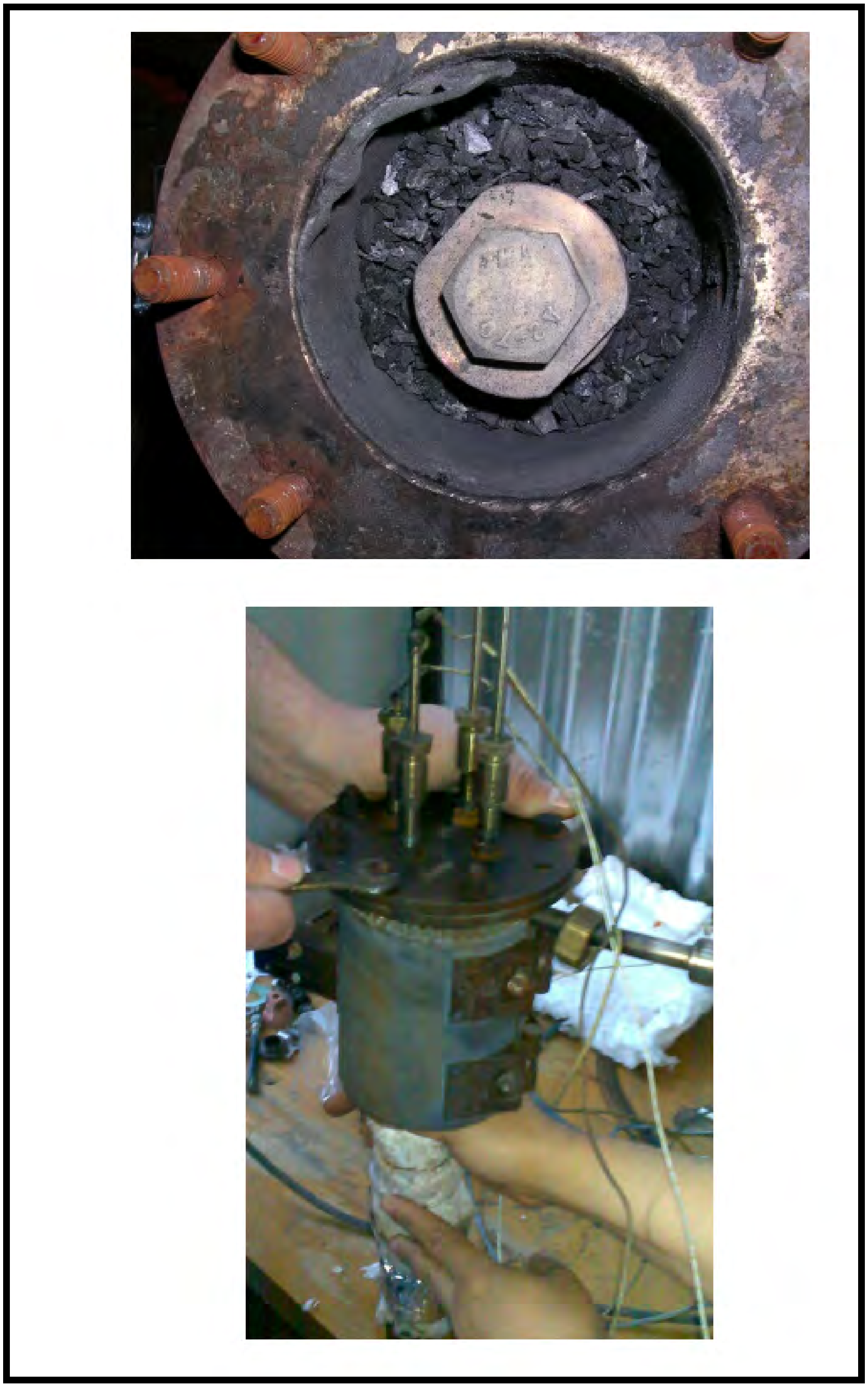


Figure 8.6 Filter filling (upper photo) and closing (lower photo) procedure

Preparations for filter installment were shown in Fig.8.7.

Figure 8.7 Filter isolation preparations for installment

Figure 8.8 Filter after installment

9. Tar and Gas Sampling Procedure

The measurement principle is based on discontinues sampling of the gas stream containing particles and condensable organic compounds. The sampling applicable approach at FSI-VUT is shown below:

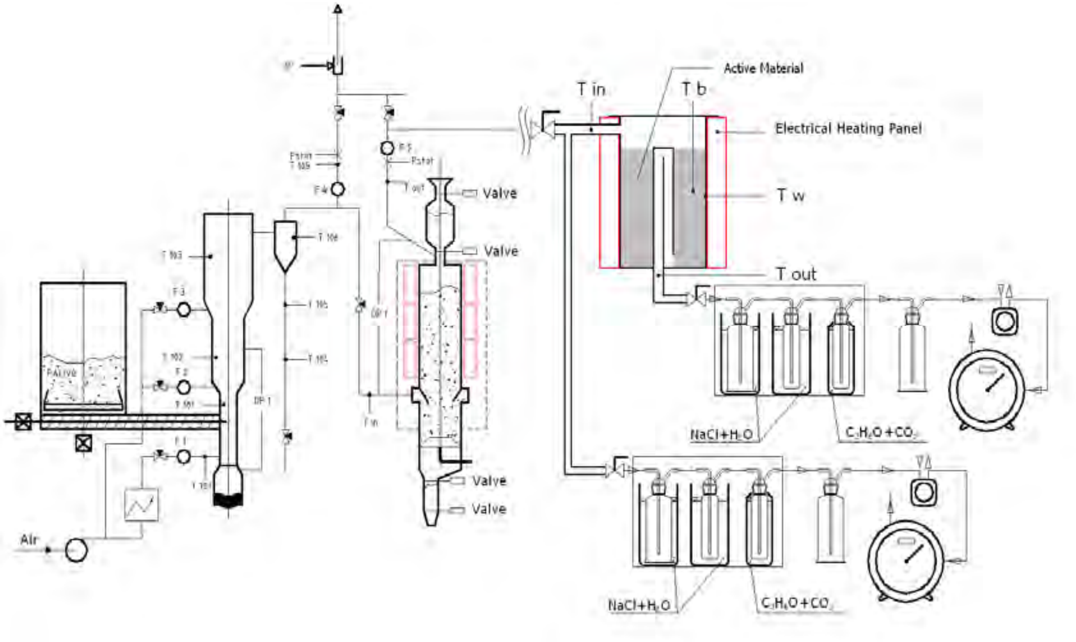


Figure 9.1 Tar sampling experimental procedure

9.1 Calculation of tar sampling conditions

According to tar protocol, the producer gas flow rate and the isokinatic sampling flow rate can be calculated from nitrogen based or carbon based mass balance. The nitrogen based balance can be applied to air – flown gasifier; the carbon based mass balance can be applied to all types of gasifiers (air – blown – and oxygen / steam gasifier. The nitrogen based method provides the actual producer gas flow rate (m^3n: normal conditions, 273.15 K, 101325 Pa = 1.01235 bar, dry basis) as the sampled gas volume is also measured as dry gas, the target isokinatic sampling flow can be controlled during sampling by monitoring and adjusting the gas meter.

The nitrogen content in the producer gas can be measured directly or as the difference of 100% of all other main producer gas components (CO, CO_2, CH_4, H_2, and H_2O).

$$q_{v,producer\ gas} = q_{v,air}\frac{N_{2air}}{N_{2,producer\ gas}}$$

Where:

$q_{v,producer\ gas}$ = Producer gas flow rate [m^3n/h]
$q_{v,air}$ = Primary air flow rate [m^3n/h]
$N_{2,air}$ = N_2 content of primary air [Vol %]
$N_{2,prodecer\ gas}$ =N_2 content of primary air [Vol %]

The carbon based method is based on a total carbon balance and can be applied when the following requirements are satisfied: Gasifier operation is stable, Main gas composition (CO, CO_2, CH_4,) is known, Fuel feeding rate (in Kg/h), fuel moisture and carbon content are known.

Solid or liquid carbonaceous stream (bottom ashes, particles, tar) and their carbon content are known. The general calculation of the producer gas flow rate based on an elemental carbon balance can be written as:

$$q_{m,fuel}\,CC_{fuel}+\sum q_{v,agent}\,CC_{agent}= q_{v,gas}\,(CC_{gas} + C_{tar}\,CC_{tar} + C_{particles}\,CC_{particles}) + q_{m,ash}\,CC_{ash}$$

Where:

$q_{m,fuel}$ = Fuel feeding rate [kg dry biomass / h]
CC_{fuel} = Carbon content of fuel [kg C / kg dry biomass] (= 0.47 for woody biomass)
$q_{v,agent}$ = Gasification agent feeding rate [m^3n/h]
CC_{agent} = Carbon content of gasification agent [kg C / m^3n]
$q_{v,gas}$ = Producer gas generation rate [m^3n/h]
CC_{gas} = Carbon content of non – condensable gases (CO, CO_2, CH_4) in producer gas [kg C / m^3n]
C_{tar} = Tar concentration in producer gas [kg C / m^3n]
CC_{tar} = Carbon content of tar [kg C / kg tar]
$C_{particles}$ = Particles concentration in producer gas [kg C / m^3n]
$CC_{particles}$ = Carbon content of particles [kg C / kg dry biomass]
$q_{m,ash}$ = Bottom ash rate [kg dry ash / h]
CC_{ash} = Carbon content of bottom ash [kg C / kg dry ash]
CC_{agent} = 0, since the gasification agent does not contain any carbonaceous gas components, except, when the bed material contain carbon containing additives like limestone.

$$Y_{gas} = \frac{q_{v,gas}}{q_{m,fuel}} = \frac{CC_{fuel} - C_{ash,fuel}\,CC_{ash}}{CC_{gas} + C_{tar}\,CC_{tar} + C_{particles}\,CC_{particles}}$$

Where:

Y_{gas} = Producer gas yield [m^3_n/ kg dry biomass]
$C_{ash,fuel}$ = Ash content of fuel [kg / kg dry biomass]

Tar compounds are divided into two different groups, the gravimetric tars and a number of individual organic compounds. The gravimetric is defined as the evaporation residue at conditions according to the temperature, pressure and duration. Individual organic compounds are not defined but those to be expected in biomass producer gases listed in a compound list in the tar measurement standards. The analysis can be performed separately depending on the type of the information required. Fig.9.2 shows tar sampling protocol and Fig. 9.3 shows the global overview of the detectability of tars with a gas chromatograph.

In the tar sampling process, a serious of four glass vessels contained ‘Acetone’ as an organic solvent connected to the pre filter tab and another serious of four vessels was connected to the filter exit tab. Both vessels serious were located in iced salted Water - Ethanol mixture in order to achieve the optimal condensation temperature.

The detailed sampling procedure for both gas and tar is shown in next pages.

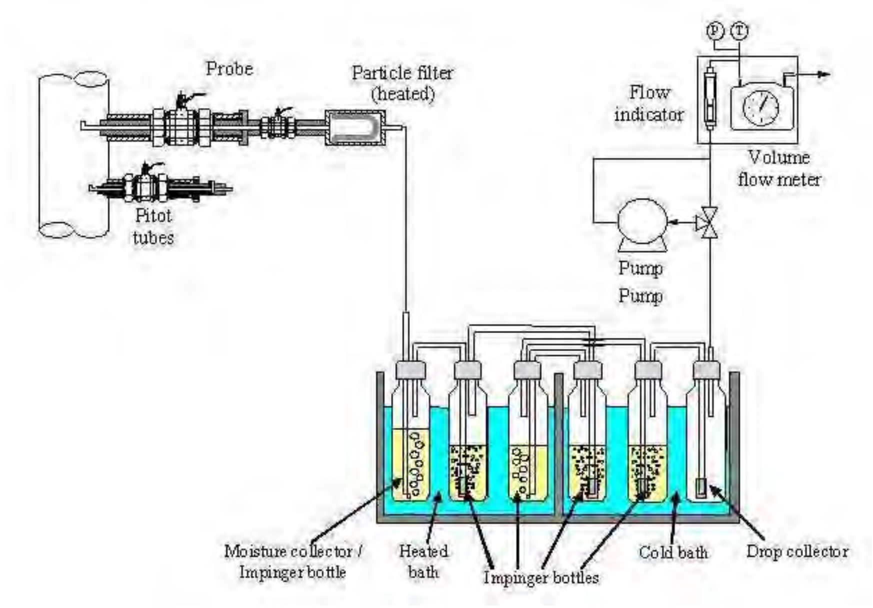


Figure 9.2 Tar sampling according to Tar Protocol

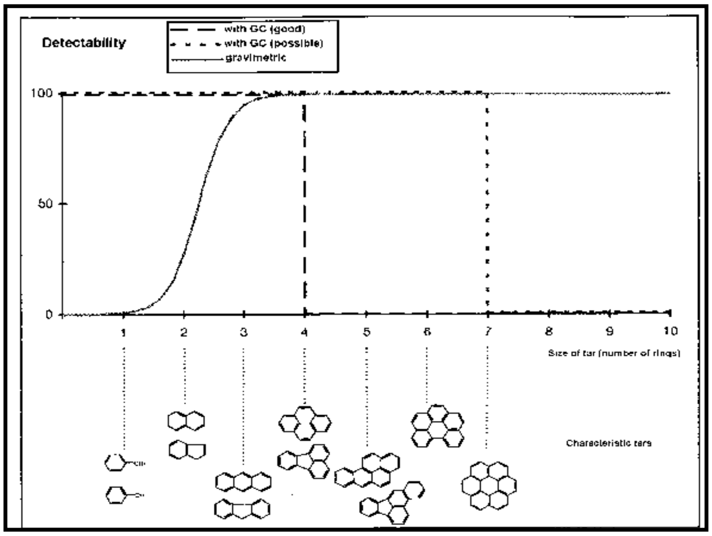


Figure 9.3 Global overview of the detectability of tars with a gas chromatograph

Figure 9.4 Tar sampling container

Figure 9.5 Tar sampling flasks

Figure 9.6 Condensation of tar during sampling

Figure.9.7 Tar samples before collection

All the experimental approach for tar sampling applied in the study is clearly shown in the Figures 9.4 – 9.8.

The final samples taken either pre or post the filter for each experiment separately were underwent an extensive tar analysis in order to indicate the total amount of each tar component. This procedure was repeated and applied for the three kinds of bed filters (Char coal, Black coke and Active carbon) for a series of different temperatures.

Figure 9.8 Collecting tar samples

During the experiment, the dolomite filter mainly traps dust particles contained in the produced gas that temperature in the dolomite catalytic fitter was about 400 ° C; this temperature is not enough for tar cracking. Fresh dolomite is fed from vessel equipped inlet periodically. The pressure drop of the filter depends on the flow rate and the filling material inserted. The gas flow rate through the HCF was (25 m^3/h) with a corresponding pressure drop of 2.5 - 3 kPa. The behavior of the pressure drop shows that it increases as the filter is clogged with dust and the development of the filter cake, If the dolomite is not partially exchanged in the filter, the filter pressure drop will increase sharply up to 10 kPa, while the gas flow rate through the filter decreases accordingly

Figure 9.9 Dolomite and Dolomite feeding inlet

9.2 Gas sampling procedure:

In order to study the producer gas achieved by the experimental series, and to investigate the concentration of different components of the gas, several gas samples has been taken during each experiment and under each set of conditions.

The gas sampling procedure comprised the replacement of the tab water by the producer gas using specified glass bottles as a sample twice, before and after the carbon filter. This operation gave the best understanding to identify the difference of composition of the gas samples before and after the carbon filter and to analyze the activity of the carbon filter during gas purification.

Figure 9.10 Gas sampling preparation (Water filling)

Figure 9.11 Ready for gas sampling

Figure 9.12 Gas sampling pre filter

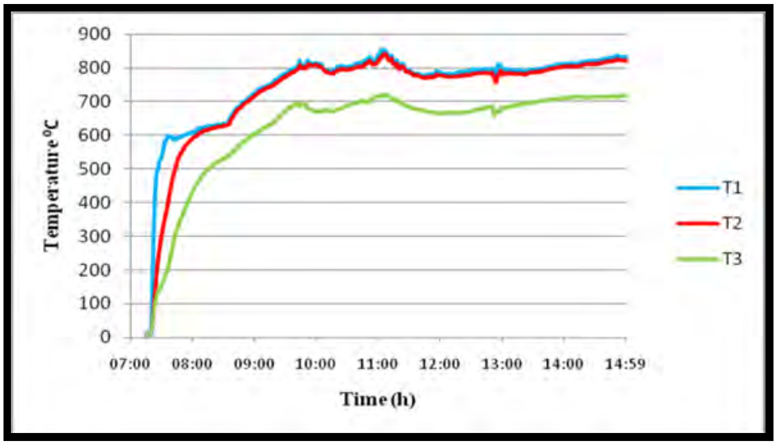
Figure.9.13 Gas sampling post filter

Figure 9.14 Final gas samples marked as pre and post filter

Figure.9.15 Final gas and tar samples

10. Results and discussion of Char coal filter

A series of data obtained through the direct monitoring of experiments. The data show that the temperature gradient along the gasifier where the gasification temperature was almost 800 ° C. The ranges of all the active temperatures around the hot catalytic filter were 300 - 400 ° C. Fig. 10.1 illustrates the temperature in the different part of the gasifier. The experimental working conditions of the char coal filter are shown in Table 10.1.



T1 = Temperature in the lowest part of the gasifier, T2 = Temperature in the central part of the gasifier
T3 = Temperature in the highest part of the gasifier

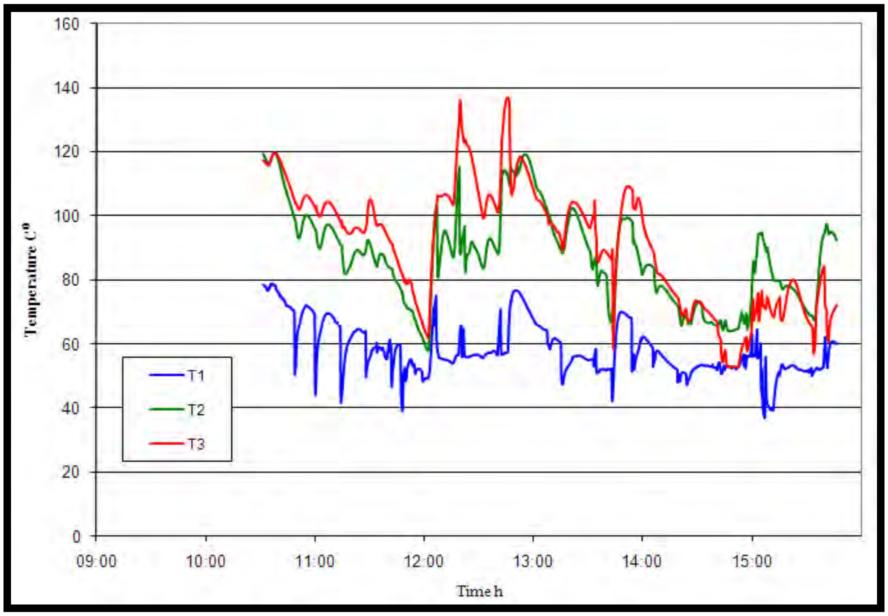
Figure 10.1 Temperature of the gasifier

Experimental conditions	
Temperature of the carbon material filter	70 - 200° C
Char coal sample weight	100 g
Char coal particle size	0.2 mm
Gas flow rate through the hot catalytic filter during sampling	5 lit/sec
Amount of gas for tar sampling	100 lit

Table 10.1 Experimental conditions of the char coal filter

Experimental temperatures in the char coal filter were selected from 70-200 ° C taking in account that it is very difficult to control the temperature inside the filter.

Fig.10.2 shows temperature in the upper, central and lower parts of the filter which were denoted as T1, T2, and T3.



T1=Temperature in the lower part of the char coal filter, T2= Temperature in the central part of the filter
T3= Temperature in the upper part of the filter

Figure.10.2 Temperatures in the parts of char coal filter

10.1 Gas samples analysis

For the range of temperatures (70 - 200 °C) the results obtained showed that the analyzed data are approximately the same which means the poor influence of temperature on gas components adsorption through the char coal filter.

Gas component	**N_2**	**CO_2**	**H_2**	**CO**	**CH_4**	**O_2**
Percentage /unit volume	50-55 %	16-18%	13-15%	8-14%	1-3%	0.12 - 0.14%

Table 10.2 Percentage of gas components post the char coal filter

In order to guarantee an optimal functioning, test equipments has been investigated for the development measurement of the main components of gas composition such as (CO, H_2, CO_2, CH_4, O_2) .The measurement of N_2, Ar, C_2H_4, C_2H_6, Benzene, toluene and xylene, are available through a complete analysis of both gas and tar analysis.

At the moment faster measurement technologies are being used for these components. This analysis has been used and done in VŠCHT.

Results of the utilization of char coal material as a bed filter show the normal gas components concentration pre and post filtration. The percentage concentration per unit volume of all components is as illustrated in Table 10.2. Graphically the gas components pre and post the char coal filter are shown in Fig 10.3. Table 10.3 shows the gas amounts pre and after the char coal filter.

Date	22/4	22/4	22/4	22/4	22/4	22/4	22/4	22/4	22/4	22/4	22/4	22/4
Time	11:53	13:08	14:00	14:20	15:02	15:42	11:53	13:05	14:00	14:20	15:02	15:42
sample	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
O2 in the sample *	0.14	0.14	0.13	0.13	0.12	0.13	0.13	0.15	0.17	0.13	0.55	0.12
CO2	18.00	16.97	16.98	16.99	16.72	16.85	17.31	16.17	15.98	16.94	16.81	16.70
H2	15.29	13.60	12.09	13.01	14.11	14.08	15.31	13.72	12.49	13.15	14.12	14.19
CO	9.93	12.03	12.11	12.31	13.30	13.12	12.47	11.93	12.30	12.33	12.87	13.05
CH4	2.55	1.88	2.53	2.65	2.76	2.79	2.70	1.84	2.56	2.65	2.71	2.78
N2	52.70	54.38	54.62	53.43	51.56	51.65	50.73	55.27	55.05	53.37	51.89	51.76
Ar	0.62	0.64	0.65	0.63	0.61	0.61	0.60	0.65	0.65	0.63	0.63	0.61
Ethane	0.115	0.056	0.093	0.087	0.078	0.078	0.102	0.051	0.096	0.086	0.079	0.078
Ethylene	0.649	0.332	0.720	0.697	0.674	0.665	0.624	0.300	0.708	0.683	0.687	0.661
acetylene	0.000	0.013	0.023	0.028	0.033	0.017	0.029	0.013	0.021	0.027	0.031	0.017
Propane	0.004	0.002	0.003	0.002	0.001	0.001	0.004	0.002	0.003	0.002	0.001	0.001
Propen	0.047	0.024	0.048	0.037	0.028	0.025	0.045	0.019	0.048	0.035	0.031	0.026
butane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,3-butadiene	0.008	0.006	0.012	0.009	0.007	0.004	0.007	0.002	0.007	0.007	0.008	0.005
1-buten-3-inch	0.000	0.002	0.004	0.004	0.003	0.002	0.003	0.001	0.004	0.003	0.004	0.003
Benzene	0.068	0.045	0.083	0.081	0.082	0.083	0.055	0.017	0.060	0.068	0.100	0.088
Toluene	0.010	0.007	0.019	0.017	0.015	0.014	0.008	0.002	0.009	0.012	0.021	0.016
others	0.011	0.005	0.007	0.008	0.006	0.006	0.010	0.003	0.006	0.007	0.005	0.005
sum	100	100	100	100	100	100	100	100	100	100	100	100
LHV MJ/m3	4.92	4.39	4.88	5.03	5.30	5.26	5.27	4.29	4.89	5.00	5.28	5.27

A= After the Filter B=Before the Filter

Table 10.3 Gas sampling average results pre and post char coal filter

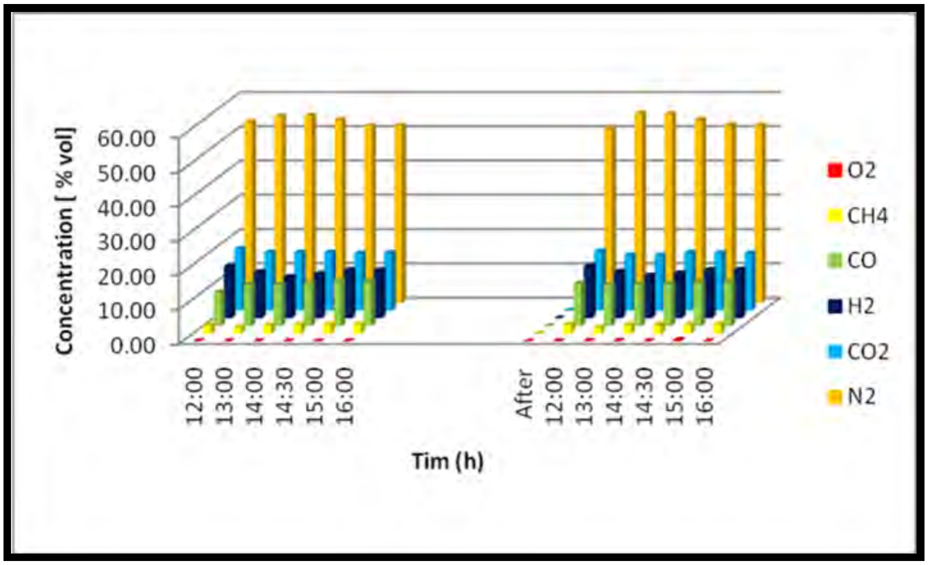


Figure 10.3 Gas components concentration per unit volume pre and post the char coal filter

Other gas components such as Ar, Ethane, Ethylene, Acethylen,Propane,Propene,Butan,1,3-butadiene,propin,Benzene,Toluene n, and the others has been studied as well and it will be referred as C_XH_Y.

These components were expressed in very small concentration per unit volume post the char coal filter, which indicates the modest ability of this carbon material for C_XH_Y absorption however the better ability for the adsorption some hydrocarbon components as will be discussed latter. The concentration of C_XH_Y gas components per unit volume are shown in Fig.10.4. The achieved resultant gas components show the ability of the charcoal carbon filter for gas purification.

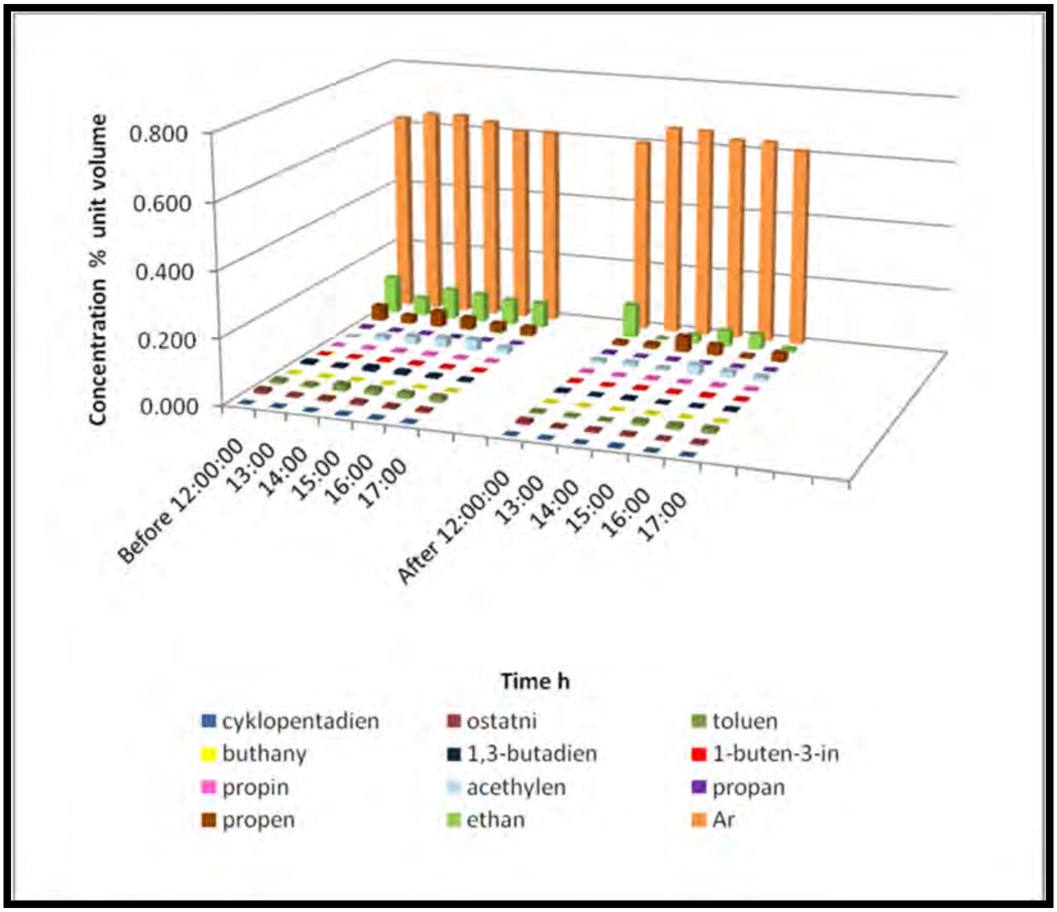


Figure 10.4 CxHy Concentration per unit volume per unit volume pre and post char coal filter

In order to study the activity of char coal for tar removal, several experiments has been achieved in different conditions, all the experiments show a gradual improvement of performance. The performance was influenced with different operational factors such as the stability of the gasification process itself and the temperatures achieved inside the carbon filter since it is very difficult to control the temperature in the various parts of the filter.

The gas low heating value has been studied pre and post the char coal filter, the study shows an approximate value of 4.8 – 5.5 MJ/$m^3$for LHV. This value considered acceptable especially that most filtration process for gas purification causes a significant drop in the gas LHV.

Fig 10.5 illustrates the low heating value pre and post the char coal filter.

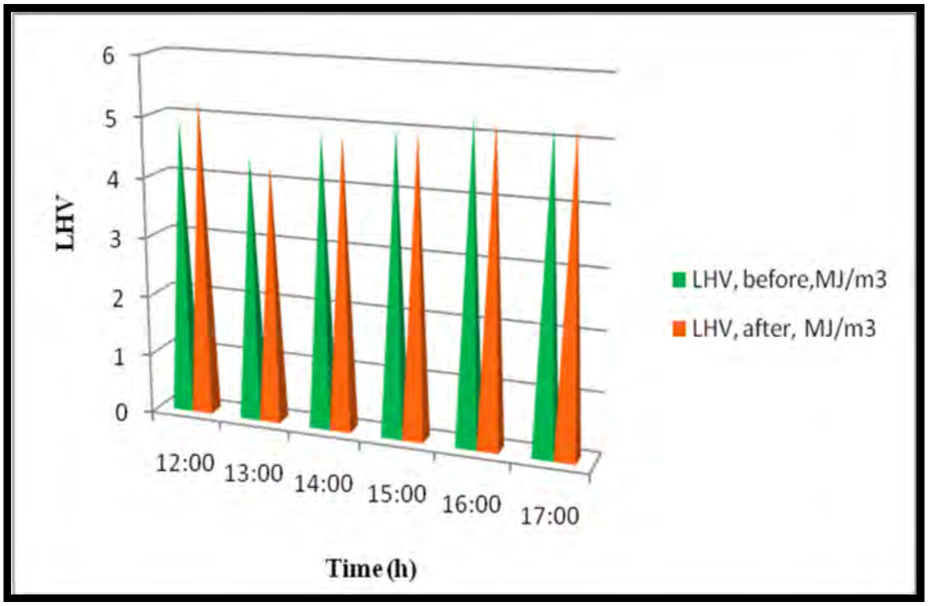


Figure 10.5 LHV (MJ/m^3) pre and post the char coal filter

10.2 Tar samples analysis

Tar can be classified to different classes depending on the nature of each class and its behavior during reactions as fellow:

- **Class II -** of tar components are the heterocyclic compounds. The components that exhibit high water solubility like Phenol, cresol, and pyridine. The value is very small or decreased to half or almost non-existent.

- **Class IV -** Light poly-aromatic hydrocarbons (2-3) rings PAHs, Naphthalene, indene, and biphenyl , these components condense at relatively high concentrations and intermediate temperatures, where it disappeared completely, except for Naphthalene which decreased to half of its concentration.

- **Class V -** Heavy poly-aromatic hydrocarbons (>4-rings PAHs), Fluoranthen, Pyrene, Chrysene, these components condense at relatively high temperature at low concentrations. Some were present and ended with a concentration equals to zero. Graphically Tar components concentration and amounts are shown in Fig.10.6 and 10.7. Table 10.4 illustrates the concentration of different tar classes' pre and post char coal filter.

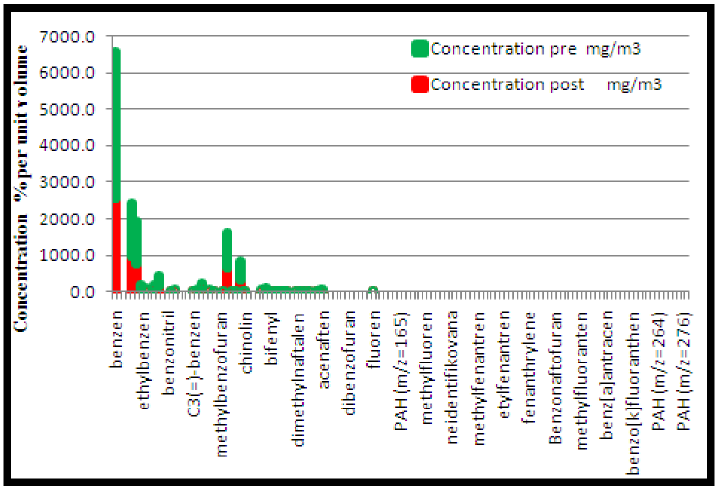


Figure 10.6 Concentration of tar components pre and post the char coal filter

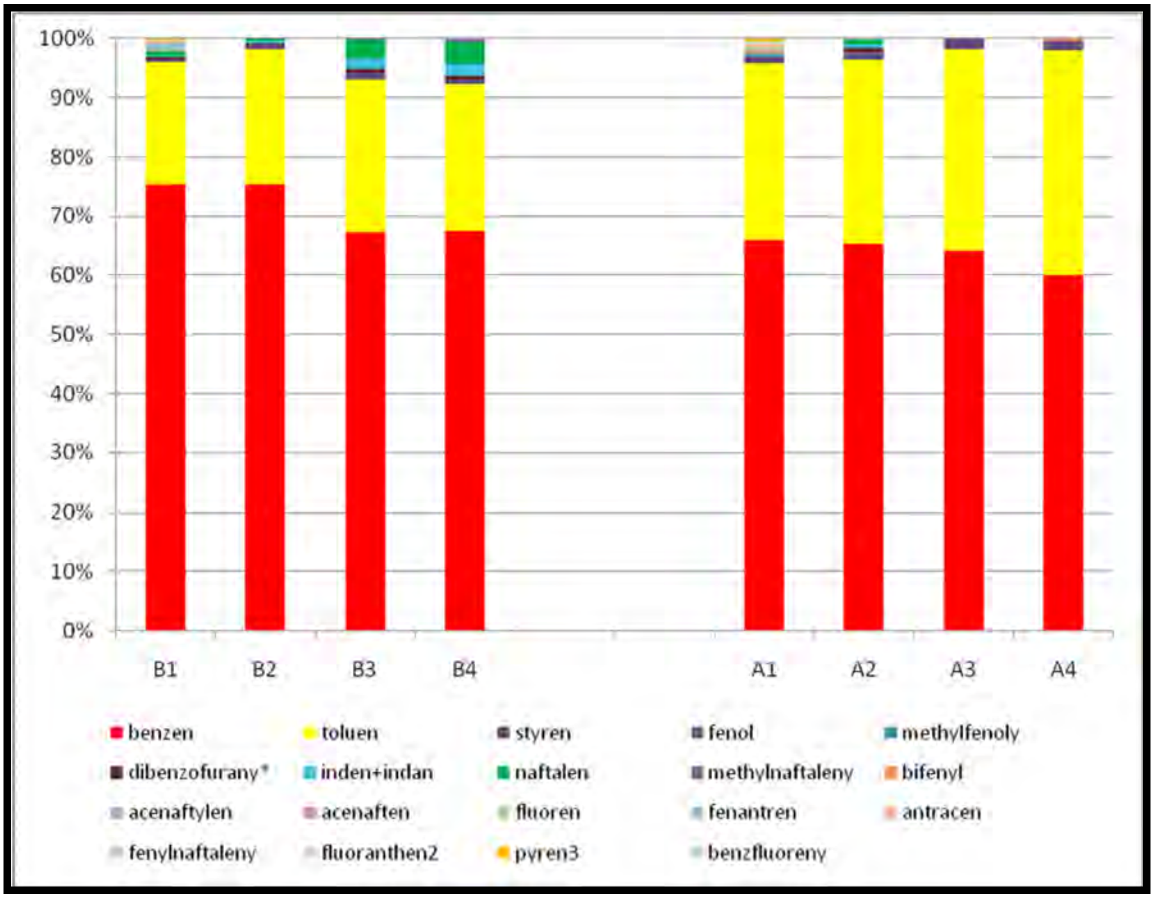
	Component	Pre-filter	Post filter	Efficiency of the filter
		Concentration mg/m^3	Concentration mg/m^3	
Class II	**Phenol**	2.7	0.0	100%
	Methyl phenol	8.7	0.0	100%
	Benzofuran	0.0	0.0	100%
	Dibenzofuran	0.0	0.0	100%
	Methylbenzofuran	0.0	0.0	100%
	Naphtha Benzofuran	0.0	0.0	100%
Class IV	**Component**	**Pre-filter**	**Post filter**	**Efficiency of the filter**
		Concentration mg/m^3	**Concentration mg/m^3**	
	Methylnaphthalene	1.0	0.8	20%
	Biphenyl	26.1	0.0	100%
	Acenaphthylene	0.0	0.0	100%
	Fluorene	0.0	0.0	100%
	Phenanthrene	0.0	0.0	100%
	Phenanthrene	0.0	0.0	100%
Class V	**Component**	**Pre-filter**	**Post filter**	**Efficiency of the filter**
		Concentration mg/m^3	**Concentration mg/m^3**	
	Fluoranthen	24.8	0.0	100%
	Pyrene	2.6	0.0	100%
	Methyl fluoranthen	0.8	0.0	100%
	Methylpyrene	0.0	0.0	100%
	Anthracene	1.0	0.0	100%
	Fluorene	0.0	0.0	100%

Table 10.4 Tar components according to classes' pre and post char coal filter

Using the char coal filter affected a wide range of tar components otherwise the concentration of Benzene and Toluene was found in higher concentration and there was no effect on these components.

According to data series obtained, it is found that the efficiency of the char coal filter ranging between 65 -75 % .Table 10.5 shows the filter efficiency as a function of filter temperature.

Fig.10.7 shows the different tar components pre and post the char coal filter.



A= After B=Before

Figure 10.7 Tar compositions per unit volume pre and post char coal filter

Gasification Temperature 800-850° C						
Char coal Filter Temperature	70°C	90°C	100°C	13°0C	150°C	200°C
Efficiency of 400 ml	69%	72%	66%	75%	74%	71%

Table 10.5 Tar removal efficiency of char coal filter as a function of filter temperature

volume of gas, l	101.0	100	100	100	100	100	100	100
Volume of acetone, ml	160	165	155	155	133	142	167	135
date	**22. 4.2008**							
Sample place:	**B1**	**B2**	**B3**	**B4**	**A1**	**A2**	**A3**	**A4**
short name	2301	2055	2572	2847	2270	1914	2898	2457
Benzene	773	699	956	1037	624	583	1111	909
Toluene	80	69	130	179	61	41	133	104

m + p + o-xylene + ethyl benzene	123	60	79	79	15	11	43	29
Styrene	104	99	171	200	34	138	204	152
C3-benzene summa	2	4	0	2	0	0	0	0
others 1	3382	2985	3908	4344	3006	2687	4388	3650
BTX summa	38	18	41	63	12	13	31	22
oxygen summa	0	1	4	22	0	6	2	0
Phenol	0	1	1	1	0	0	0	0
methyl phenol	38	13	36	39	12	7	28	22
Dibenzofuran *	0	2	0	2	0	0	0	0
Nitrogen	85	33	117	147	6	8	77	73
inden + indane	320	110	334	354	21	9	130	134
naphthalene	41	12	74	85	2	0	11	16
methylnaphthalene	5	4	17	27	0	0	0	4
ALKYLNAPHTHALENES (Alkyl> = C2)	2	1	5	8	1	0	0	2
biphenyl	5	3	10	14	3	0	1	1
acenaphtylene	8	4	27	41	3	0	1	4
acenaphtene	3	0	0	3	9	0	0	0
fluorene	3	0	0	3	1	0	0	0
PAH o M / Z = 165.166	13	1	0	0	29	1	0	0
Phenanthrene	5	1	0	0	7	0	0	0
anthracene	4	0	0	0	7	0	0	0
methylfenantren 4 H-cyclopenta [def] Phenanthrene	1	0	0	0	2	0	0	0
fenylnaftaleny	2	0	0	0	5	0	0	0
fluoranthen2	3	0	0	0	6	0	0	0
pyren3	0	0	0	0	0	0	0	0
benzfluoreny	0	0	0	0	0	0	0	0
methylfluoranten + methylpyrene	0	0	0	0	1	0	0	0
PAH circles of 4 ** (m / z = 226.228)	0	0	0	0	0	0	0	0
summa tar (non-BTX)	554.4	198	638	759	120	34	256	260

Table 10.6 Tar sampling average results per unit volume pre and post char coal filter

If Benzene will not be considered as a PAH substance, then the concentration of the other different tar components created during the gasification process possible to be shown in Fig.10.8.

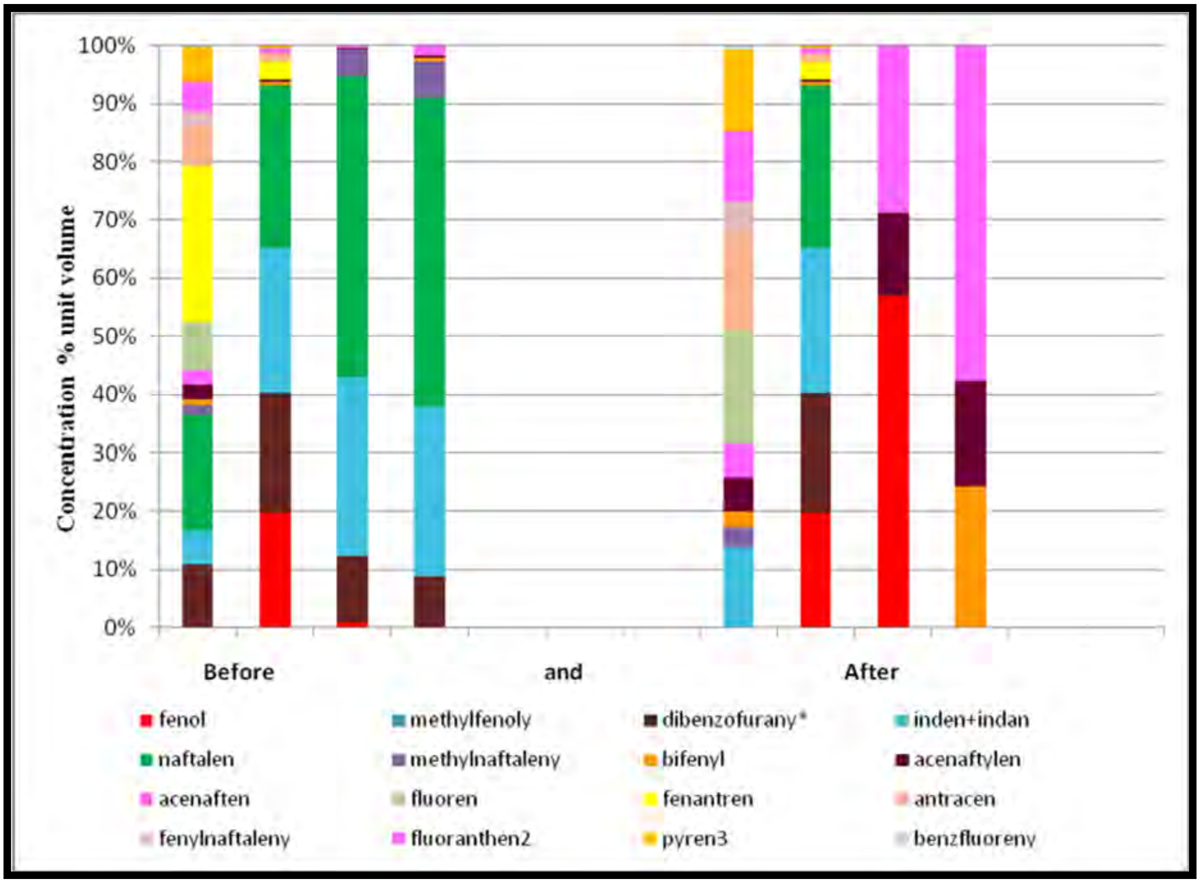


Figure 10.8 Tar compositions per unit volume pre and post char coal filter without Benzene

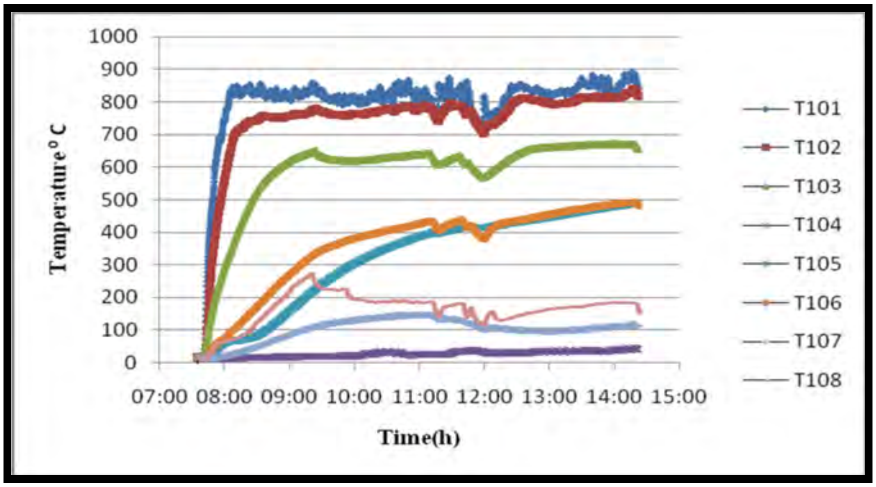
11. Results and discussion of Black coke filter

Following the same procedure included the experimental conditions for both gas and tar sampling; the black coke filter has been tested.

The optimal gasification temperature in was 800-900° C where the hot catalytic filter temperature performed around 300-400 °C. The temperature operating black coke filter was 70-200 °C.

The pressure inside the fuel reservoir and the outlet gas was approximately 10-12 kPa where the pressure drop in fluidized bed and the hot catalytic filter were extremely 100 Pa.

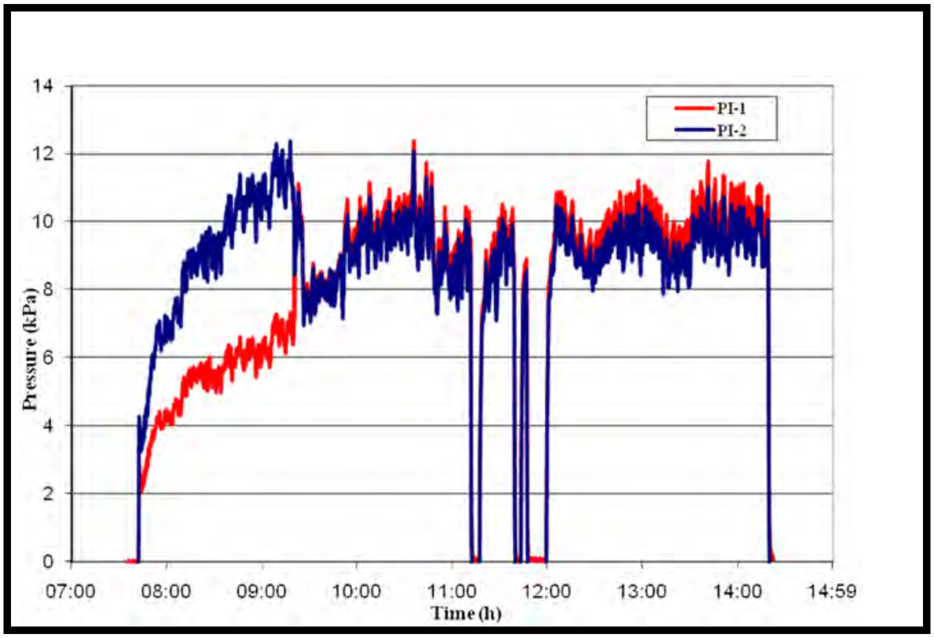
Fig 11.1 shows all the temperature profile during the experiment.



T101 – T108 = Temperatures along the gasification plant (Fig.7.1).

Figure 11.1 Temperatures Profile of the gasifier

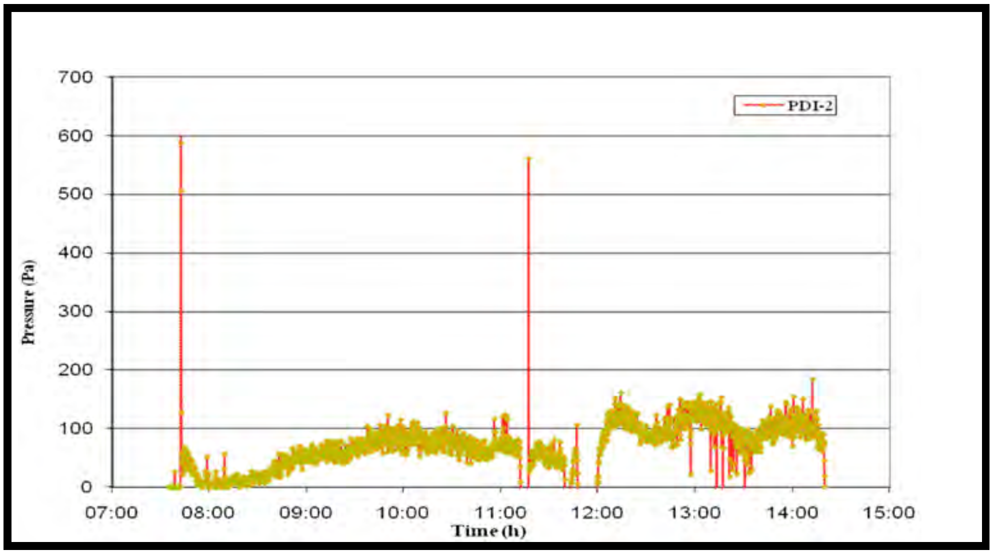
Fig 11.2 shows pressure of the outlet gas and the fuel reservoir, Fig. 11.3 Pressure lost in the fluidized bed, Fig. 11.4 shows Pressure drop in the hot catalytic filter.



PI-1= Pressure on outlet from gasifire
PI-2= Pressure in fuel reservoir

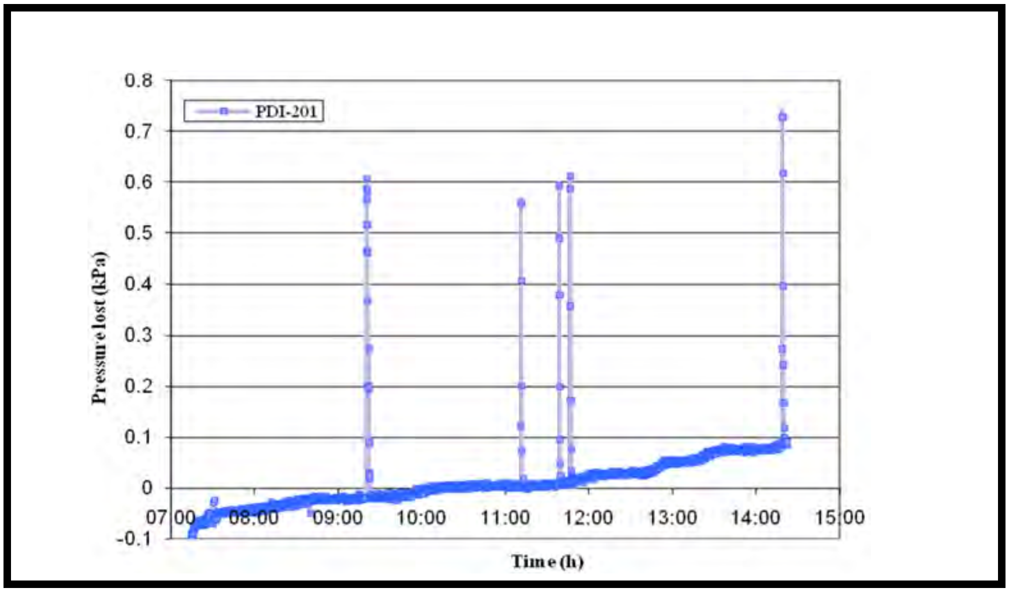
Figure 11.2 Pressure of the outlet gas and the fuel reservoir

In the above figure it was shown some points of drastic drop in pressure, these points are actually due to either turning off the gasifier after a sudden serious hazard signal or due to mistakes during monitoring however these points does not affect the final results, both pressures were kept in acceptable level.



PDI-2 = Pressure lost of the fluidized bed

Figure 11.3 Pressure lost in the fluidized bed

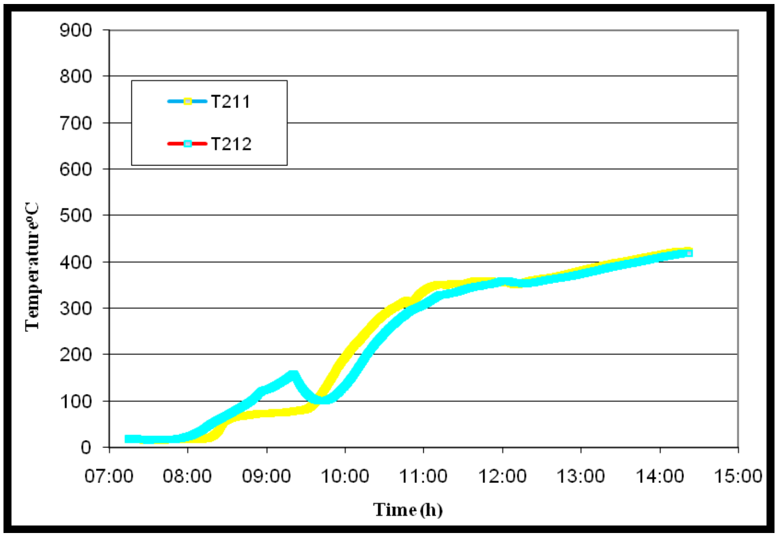


PDI-201 = Pressure lost of the hot catalytic filter

Figure 11.4 Pressure lost in the hot catalytic filter

In both Figure 11.3 and Figure 11.4, it is shown that some error points have been occurred during the testing procedure either because the feeding or changing the amount of the dolomite material each 30 minutes and causes an operating of the rotary grate.

These points are negligible since it has no effect on the normal presented curve.

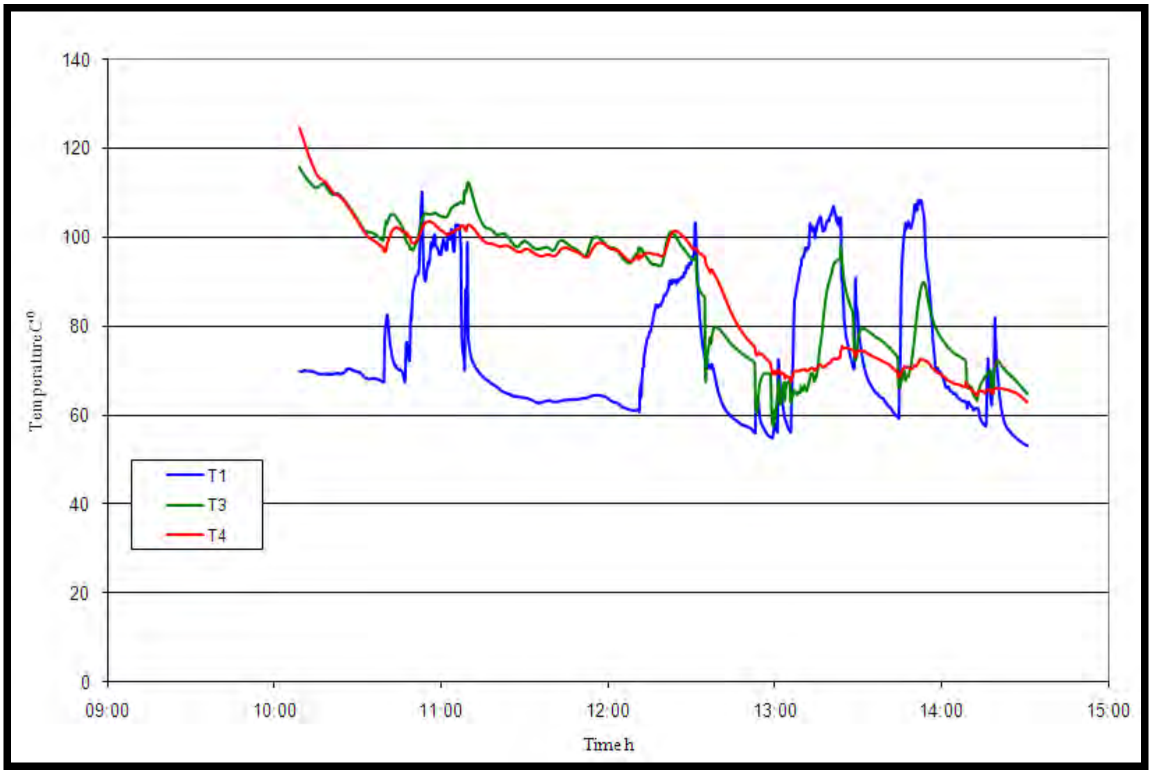


T211, T212 = Temperatures in upper and lower parts of the hot catalytic filter

Figure 11.5 Temperatures in the hot catalytic filter

It is shown that the temperature of the hot catalytic filter is almost 400 °C, which is not nearly enough for tar cracking and for this reason; the dolomite bed filter has been used as a dust trapper.

The temperatures in the various parts of the black coke filter were recorded between 70 - 200 °C. Fig. 11.6 illustrates the variation of temperature inside this filter. It is clear that the temperature T1 inside the black coke was not stable ranging from 60-120°C. This instability is showing clearly the gas and tar sampling procedure effect.



T1=Temperature in the upper part of the filter (inlet gas)

T2= Temperature in the central part of the filter, T3= Temperature in the lower part of the filter (the catalytic filter)

Figure.11.6 Temperature inside the black coke filter

11.1 Gas samples analysis:

Black coke filter show a slight activity for adsorption of the formative different gas components although the large surface area of the material particles and the fair experimental conditions. The concentration per unit volume for O_2, CO2, H_2, CO, CH_4 and N_2 pre and post the black coke filter is shown in Table 11.1 and the gas composition pre and post the black coke filter is shown in Fig.11.7.

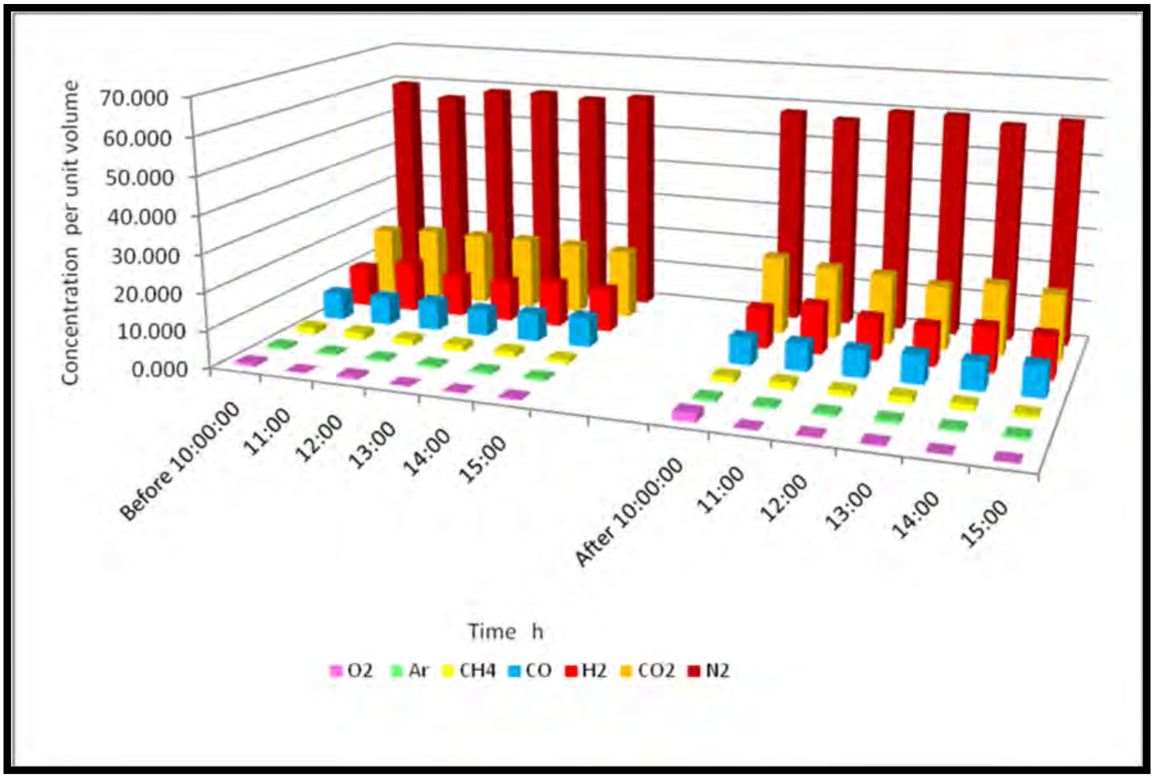


Figure 11.7 Gas compositions per unit volume pre and post black coke filter per unit volume

Other gas components which were referred to as C_XH_Y were performed in very small concentrations, Ar, Ethylene and Propen recorded the highest concentration. Fig.11.8 shows the concentration of C_XH_Y pre and post the black coke filter.

It is very common to have massive amounts of some components of CxHy due the tar destruction during the gasification process; this is visible in the components like Ethan, Ethylene and Butadiene.

Table 11.2 show the gas sampling analysis pre and post black coke filter.

Gas component	N_2	CO_2	H_2	O_2	CO	CH_4
Percentage /unit volume	55- 60 %	18-22%	10-12 %	2-5 %	5-8 %	1-3%

Table 11.1 Percentage of gas components post the black coke filter

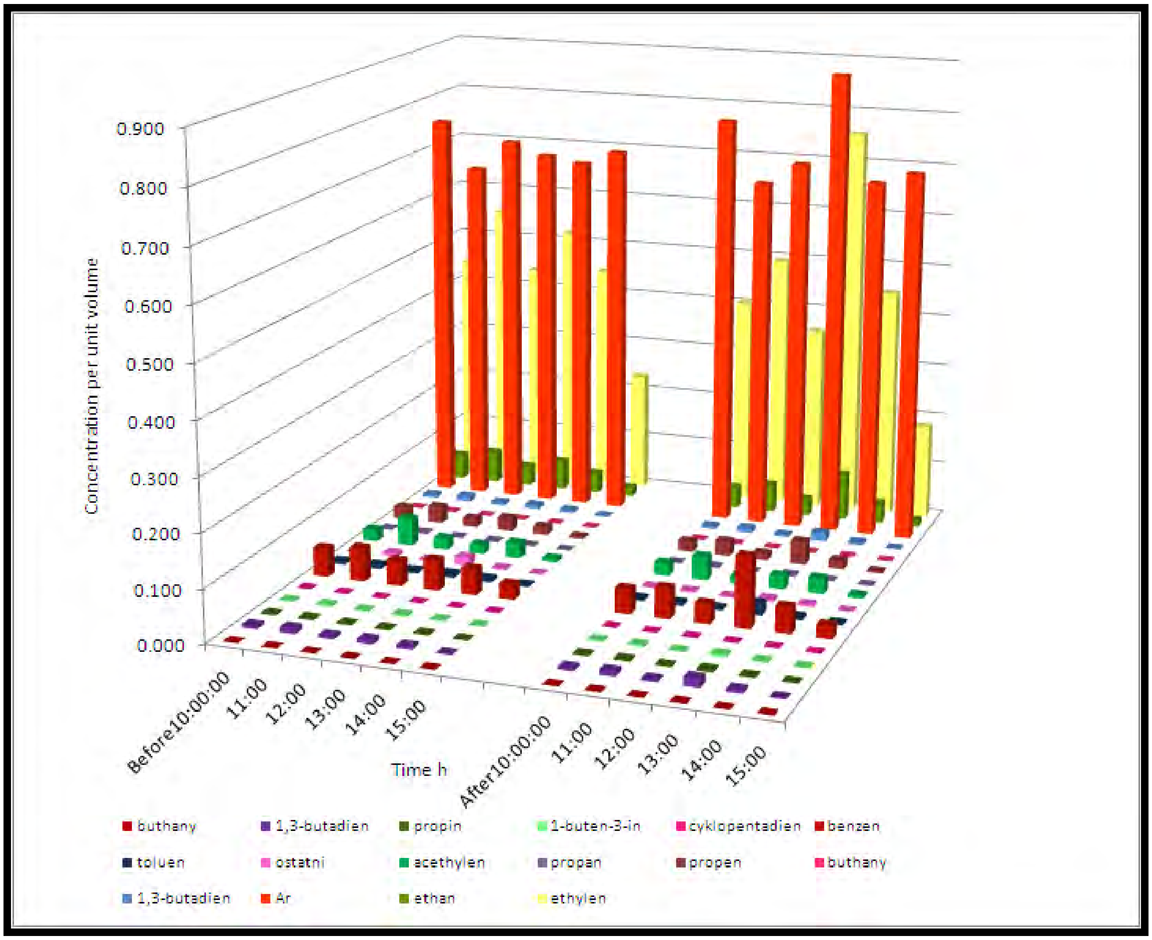


Figure 11.8 Concentration of C_XH_Y pre and post the black coke filter per unit volume

Where the average LHV for the gas is equals to 4 - 7 MJ/m^3, the gas LHV pre and post the black coke filter was ranging in between 3 - 4 MJ/m^3, which is lower, compared to the previous experiment using the char coal filter.

However the black coke filter does not cause a dramatic drop in the LHV which usually accrues during gas cleaning procedure.

Fig 11.9 shows the gas LHV pre and post the black coke filter.

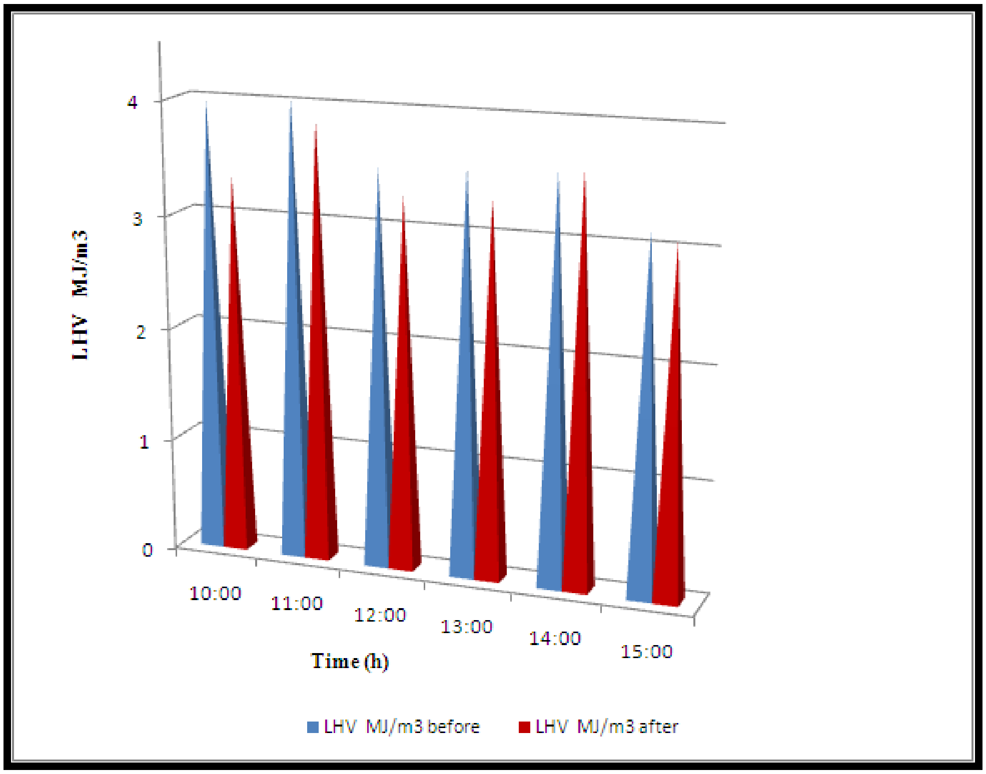


Figure 11.9 Low heating value pre and post the black coke filter

Time	10:40	11:10	12:35	12:53	13:28	14:20	10:40	11:10	11:10	12:53	13:28	14:20
Sample	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
O2	0.890	0.158	0.762	0.156	0.155	0.397	2.242	0.176	0.342	0.450	0.157	0.171
CO2	18.354	19.380	19.211	19.328	19.152	18.610	20.913	19.363	18.817	17.251	19.099	18.087
H2	10.880	13.452	11.152	11.193	12.102	11.692	10.815	13.249	11.430	10.852	12.200	11.558
CO	7.392	7.625	7.911	7.091	7.568	7.965	7.249	7.358	7.315	7.780	7.589	8.398
CH4	1.649	1.926	1.638	1.729	1.591	1.092	1.610	1.789	1.409	1.734	1.602	0.920
N2	59.472	56.159	58.787	59.244	58.299	59.632	58.074	56.863	59.846	59.939	58.221	60.092
Ar**	0.756	0.666	0.724	0.702	0.691	0.717	0.791	0.675	0.717	0.890	0.690	0.712
Ethan	0.049	0.062	0.039	0.058	0.040	0.017	0.041	0.055	0.033	0.090	0.040	0.013
ethylene	0.440	0.551	0.436	0.518	0.444	0.231	0.402	0.494	0.357	0.755	0.446	0.183
acetylene	0.022	0.053	0.022	0.017	0.029	0.007	0.024	0.045	0.015	0.025	0.029	0.005
propane	0.001	0.002	0.001	0.002	0.001	0.000	0.001	0.002	0.001	0.003	0.001	0.000
Propen	0.023	0.032	0.016	0.025	0.016	0.004	0.020	0.028	0.012	0.045	0.016	0.003
butane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,3-butadien	0.006	0.010	0.005	0.008	0.005	0.001	0.005	0.009	0.004	0.016	0.005	0.001
propane	0.002	0.003	0.002	0.002	0.002	0.000	0.002	0.003	0.001	0.004	0.002	0.000
1-buten-3-in	0.002	0.003	0.002	0.002	0.002	0.000	0.002	0.003	0.001	0.004	0.002	0.000
cyklopentadien	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
benzene	0.055	0.064	0.048	0.058	0.050	0.029	0.047	0.057	0.037	0.134	0.049	0.024
toluene	0.006	0.007	0.005	0.008	0.007	0.003	0.004	0.005	0.004	0.022	0.006	0.002
ostatni	0.001	0.006	0.001	0.016	0.002	0.000	0.001	0.003	0.001	0.005	0.003	0.000
suma	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
LHV,MJ/m3	4.010	4.053	3.508	3.564	3.585	3.152	3.352	3.867	3.292	3.311	3.605	3.077

A= After B=Before

Table 11.2 Gas sampling analysis pre and post black coke filter

11.2 Tar samples analysis:

Tar samples analysis pre and post black coke filter show ineffectiveness of this material for tar removal. For all tar classes it was found that no significant change either in amounts or concentrations.

Table 12.3 shows concentration of tar classes pre and post the black coke filter.

In order to study the effect of the filter on tar adsorption four experiments has been done and it was found out that even in low temperature, the different tar classes variation pre and post filter took very small range of variation and this did not affect the amounts of PAH and the components which appeared in very low concentration pre filter kept the same concentration post the filter.

Class II	**Component**	**Pre-filter**	**Post filter**	**filter Efficiency %**
		Concentration mg/m^3		
	Phenol	0.0	0.0	100%
	Methyl phenol	0.0	0.0	100%
	Benzofuran	41.6	30.0	25%
	Dibenzofuran	8.4	6.1	25%
	Methylbenzofuran	1.4	1.0	93%
	NaphthaBenzofuran	45.9	33.1	27%
Class IV	**Component**	**Pre-filter**	**Post filter**	**filter Efficiency %**
		Concentration mg/m^3		
	Methylnaphthalene	0.9	0.6	44%
	Biphenyl	29.4	21.2	11%
	Acenaphthylene	0.0	0.0	100%
	Fluorene	47.1	34.0	60%
	Phenanthrene	2.5	1.8	68%
	Phenanthrene	0.0	0.0	100%
Class V	**Component**	**Pre-filter**	**Post filter**	**filter Efficiency %**
		Concentration mg/m^3		
	Fluoranthen	0.4	0.3	100%
	Pyrene	0.0	0.0	100%
	Methyl fluoranthen	4.1	3.0	100%
	Methylpyrene	4.5	0.4	100%
	Anthracene	0.0	0.0	100%
	Fluorene	2.2	0.2	100%

Table 11.3 Concentration of tar classes and the filter efficiency for tar removal pre and post the black coke filter

The black coke filter shows a poor ability for the cracking of Benzene, Toluene and Naphthalene. It was shown that the concentrations of these materials still in the high level of close to the conditions pre filter as shown in Figure 11.10.

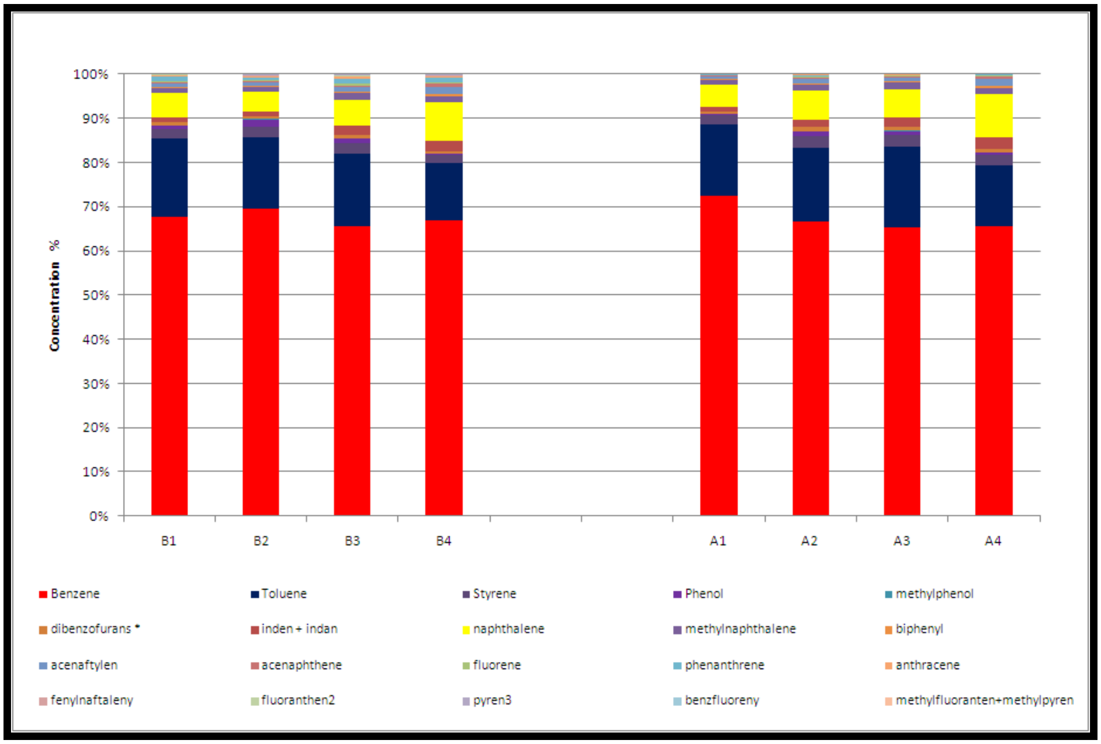


Figure 11.10 Tar composition pre and post black coke filter

Fig. 11.11 shows the tar components without Benzene. It is shown that only a small amount of Phenol has been adsorbed, the only obvious change has been accrued on the Phenanthrene.

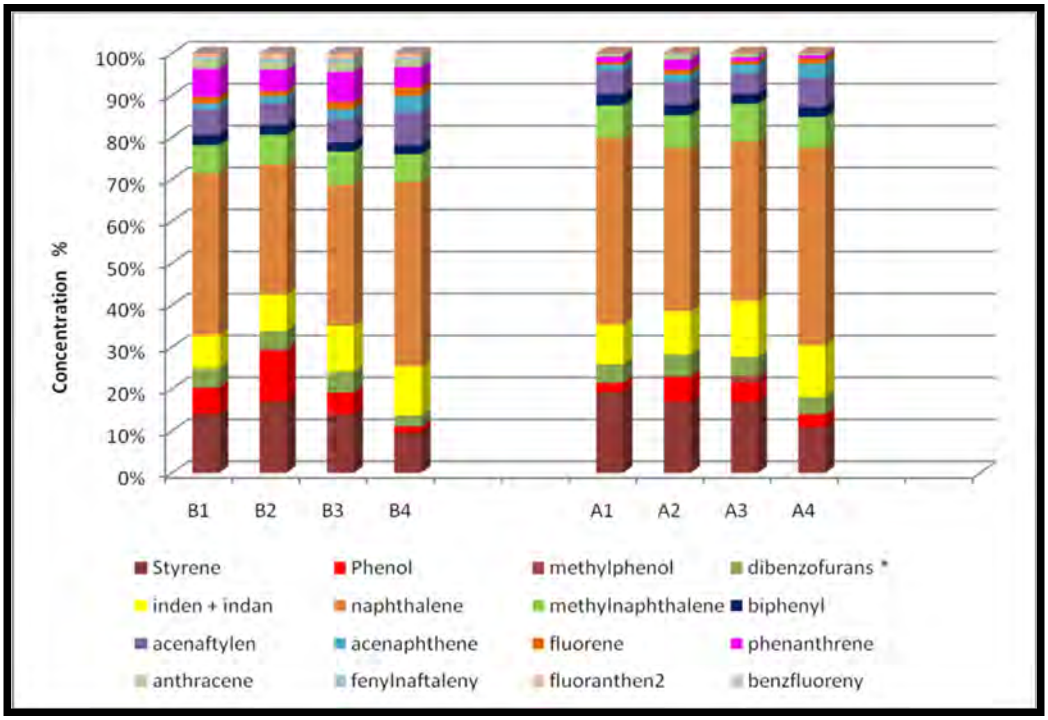


Figure 11.11 Tar composition without Benzene pre and post black coke filter

Description / start collecting	10:40-11:06	12:15-12:35	13:10-13:40	13:50-14:30	10:47-11:06	12:15-12:25	13:10-13:40	13:50-14:30
sample (marked)	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008
volume of gas, l	102.0	101.0	120.0	100.0	126.0	105.0	150.0	100.0
Volume of acetone, ml	184	140	180	152	205	139	170	136
date	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008	27/05/2008
taking place:	**B1**	**B2**	**B3**	**B4**	**A1**	**A2**	**A3**	**A4**
Benzene	1604	1233	1778	1989	1832	1392	1893	2000
Toluene	420	281	440	380	405	347	533	425
m + p + o-xylene + ethylbenzene + phenylethyn	21	23	35	27	23	30	42	30
Styrene	48	43	68	57	56	59	81	69
C3-benzene summa (nas + NENAs)	10	15	18	16	7	15	32	31
others 1	0	0	1	1	1	1	0	0
BTX summa	2103	1596	2339	2471	2325	1844	2580	2556
Oxygen summa	37	42	50	24	20	40	52	46
Phenol	21	30	25	8	6	21	22	19
Sample	B1	B2	B3	B4	A1	A2	A3	A4
methyl phenol	1	2	0	1	0	1	8	1
Dibenzofuran *	15	11	24	16	13	18	22	26
Nitrogen	0	0	1	0	1	1	0	0
inden + indane	28	22	53	69	28	36	63	78
naphthalene	132	78	163	262	129	137	182	297
methylnaphthalene	23	18	38	39	23	27	44	47
ALKYLNAPHTHALENES (Alkyl> = C2)	13	5	17	21	5	9	14	11
biphenyl	8	6	10	13	8	8	11	15
Acenaphthylene	20	13	27	46	16	19	24	44
acenaphtene	5	4	11	23	4	6	10	22
fluorene	5	3	9	13	2	4	4	8
PAH o M / Z = 165.166	5	2	7	8	1	2	2	2
Phenanthrene	23	13	35	29	4	8	4	4
anthracene	8	5	11	11	2	4	3	2
methylfenantren 4 H-cyclopenta [def] Phenanthrene	4	3	10	8	0	1	1	0
fenylnaftaleny	2	2	4	3	0	0	1	0
fluoranthen2	3	3	7	6	0	0	1	0
pyren3	3	3	6	6	0	1	1	0
benzfluoreny	0	0	0	0	0	0	0	0
methylfluoranten+methylpyren	0	0	0	0	0	0	0	0
PAH o 4 kruzich (m/z=226,228)**	1	0	1	1	0	0	0	0
summa tar (non-BTX)	330.3	232.2	469.4	591.6	246.0	314.7	425.8	587.0

A= After B= Before

Table 11.4 Tar analysis pre and post black coke filter

A summary of the results obtained using black coke filter is shown in Table 11.4 and the efficiency in different operating temperatures illustrated in Table 11.5.

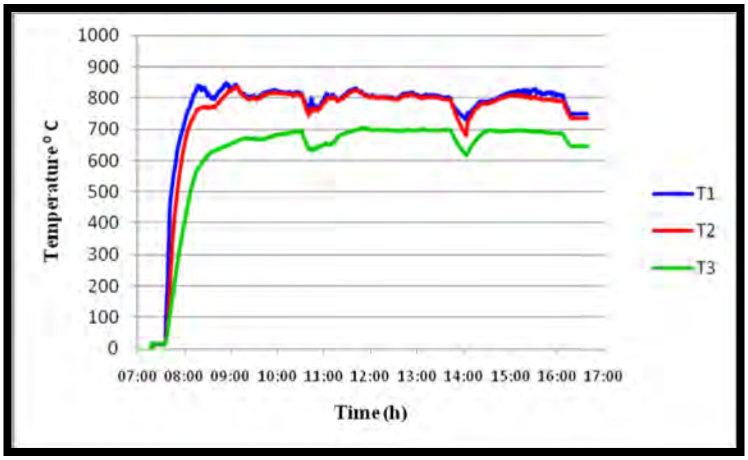
Gasification Temperature 800-850 °C						
Black coke Filter Temperature	70°C	90°C	100°C	130°C	150°C	200°C
Efficiency of 400 ml	55%	46%	51%	48%	52%	51%

Table 11.5 Black coke filter efficiency as a function of filter temperature

12. Results and discussion of Active carbon Filter

A series of experimental studies has been done on the active carbon material as a filter through the biomass gasification process. All the experiments show the successful and efficient utilization of this material.

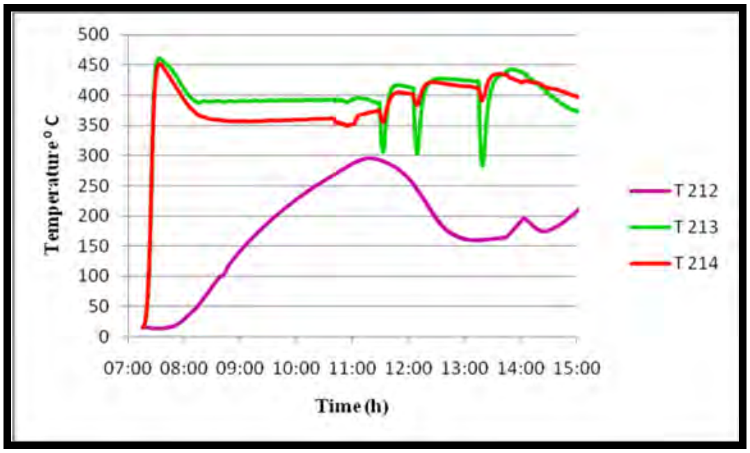
Temperatures in the different part of the gasifier 800-850 °C as shown in Fig.12.1



T1=Temperature in the upper part of the gasifier, T2=Temperature of central part of the gasifier
T3=Temperature in the lower part of the gasifier

Figure 12.1 Temperature in the different part of gasifier

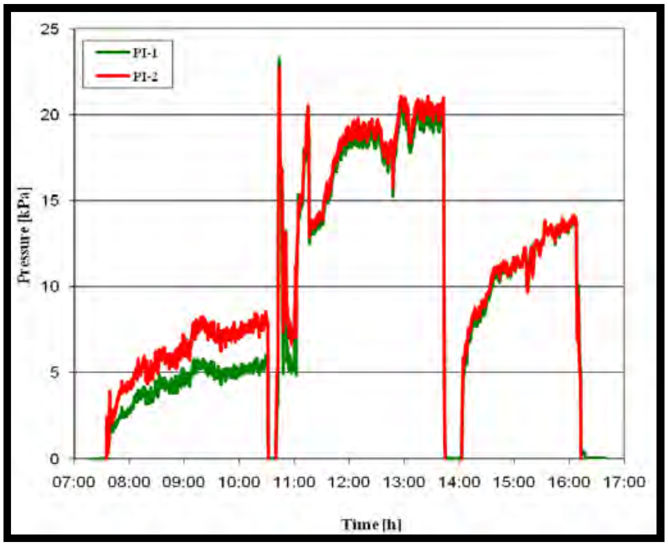
Where the temperaturs inside the different parts of hot catalytic filter were 300-450 °C as shown in Fig.12.2.



T212= Temperature in the lowest part of the reactor, T213= Temperature in the middle part of the reactor.
T214= Temperature in the upper part of the reactor,

Figure 12.2 Temperatures of the hot catalytic filter

The pressure of the fuel reservoir and the pressure of gas in outlet of the gasifier were approximately the same. The peak record of both was about 20 kPa as shown in Fig.12.3.



PI-1= Pressure lost of the fuel resevior
PI-2= Pressure lost of outlet gas

Figure 12.3 Pressure of the fuel reservoir and gas in outlet of the gasifier

The pressure lost through the gasification plant was roughly 1 kPa as shown in Fig.12.4

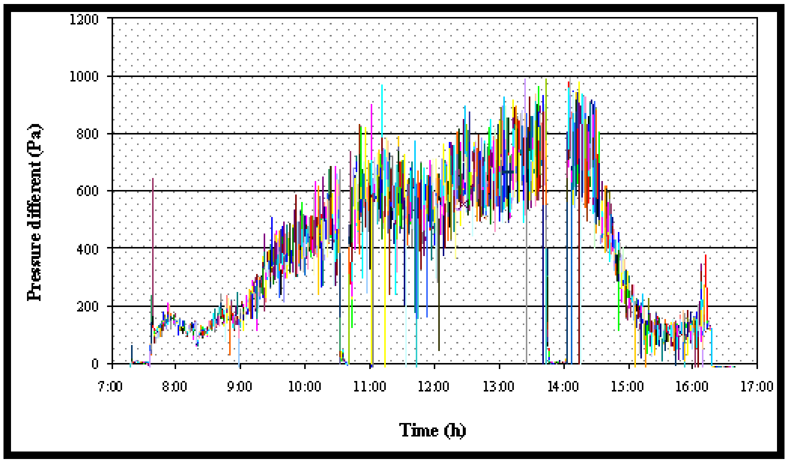


Figure 12.4 Pressure lost through the gasification plant

The temperature in the central part of the active carbon filter which is denoted by T3 was recorded between 75-105 °C as shows in Fig.12.5. (Note: T1 and T3 inside the active carbon filter has been lost due to some error in the monitering system during the experemital work.)

Gas component	**N_2**	**CO_2**	**H_2**	**CO**	**CH_4**	**O_2**
Percentage /unit volume	55-59 %	16-20%	10-16%	8-14%	1-3%	0.12 - 0.14%

Table 12.1 Gas composition post active carbon filter

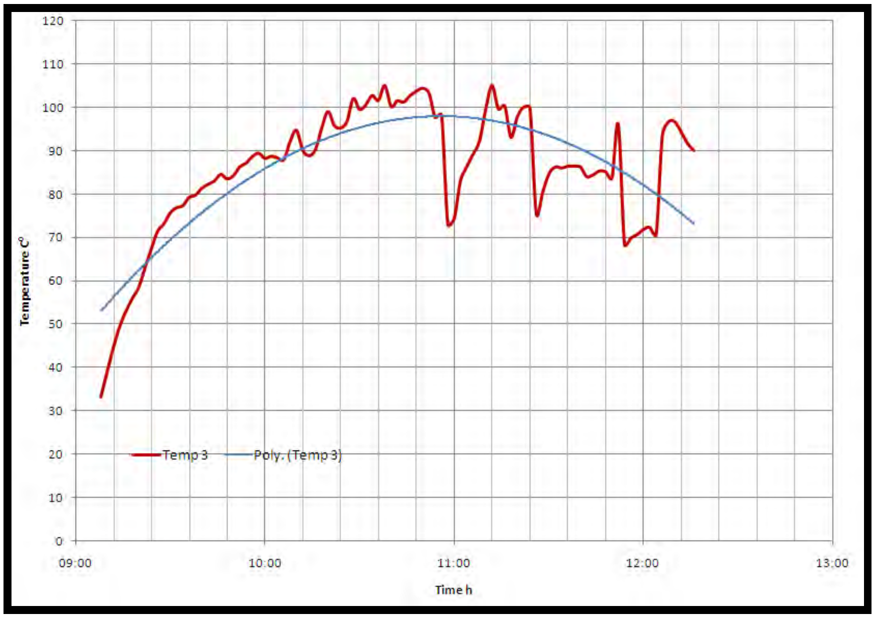


Figure 12.5 Temperature in the central part of the active carbon filter

12.1 Gas samples analysis

Analysis of gas using the active carbon filter show diffrent results for each of the formative component where the amounts of CO,CO_2 and CH_4 has been influinced by the filter and the persentage concentration has been decreased by 5 - 10% , the concentration of other components remain in the same level before and after the filter. Table 12.1 illustrates the percentage of gas components using the active carbon filter.

Fig 12.6 shows the gas composition pre and post the active carbon filter.

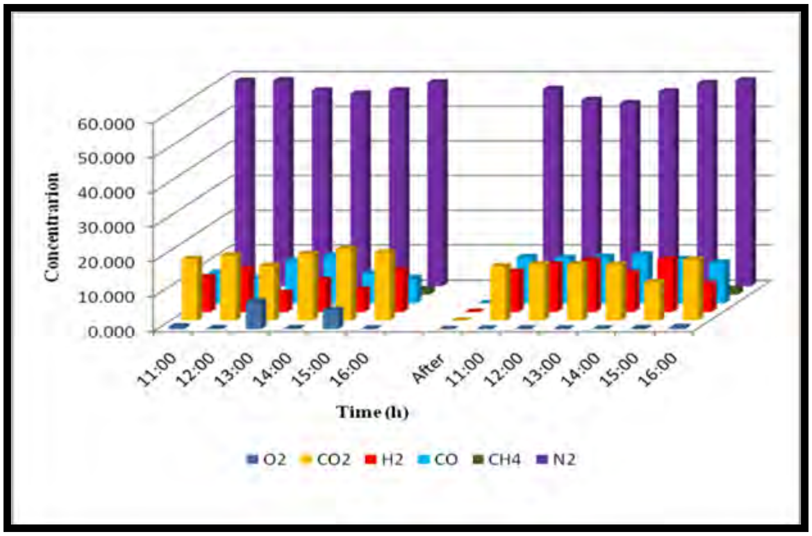


Figure 12.6 Gas composition concentrations per unit volume pre and post active carbon filter

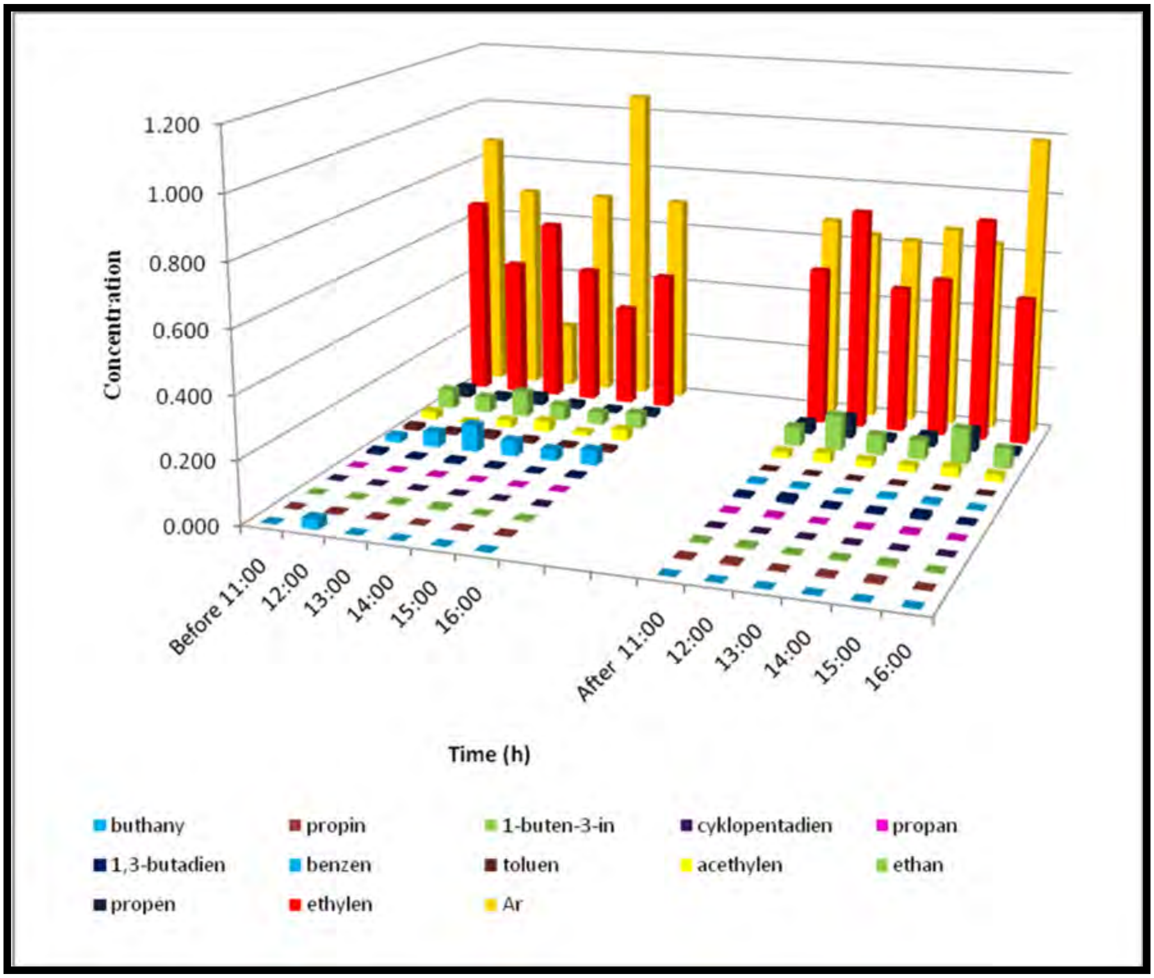


Figure 12.7 Concentration per unit volume of C_xH_y pre and post active carbon filter

Sample	before	before	before	before	before	before	After	After	After	After	After	After
O2	0.740	0.250	7.931	0.290	5.576	0.145	0.142	0.130	0.138	0.150	0.290	0.590
CO2	17.596	18.542	15.546	18.989	20.431	19.444	15.42	16.04	16.00	15.85	11.05	17.35
H2	9.813	12.200	5.465	9.124	6.443	11.905	11.42	13.50	14.59	10.98	14.98	8.135
CO	8.564	7.023	12.181	13.700	8.418	7.071	13.09	12.91	13.22	13.86	12.56	11.54
CH4	2.564	1.522	1.563	1.265	1.364	1.537	2.022	2.394	2.361	1.840	1.120	1.654
N2	59.00	59.120	56.218	55.289	56.254	58.556	56.68	53.50	52.58	55.95	58.35	59.12
Ar**	0.87	0.695	0.215	0.695	1.057	0.695	0.671	0.633	0.623	0.671	0.633	0.987
Ethan	0.06	0.052	0.084	0.052	0.041	0.052	0.063	0.117	0.065	0.063	0.117	0.065
ethylene	0.66	0.459	0.611	0.459	0.335	0.459	0.529	0.738	0.488	0.529	0.738	0.488
acetylene	0.02	0.003	0.024	0.036	0.012	0.036	0.022	0.031	0.023	0.022	0.031	0.023
propane	0.00	0.001	0.002	0.001	0.001	0.001	0.002	0.005	0.001	0.002	0.005	0.001
Propen	0.036	0.020	0.033	0.020	0.013	0.020	0.040	0.073	0.019	0.040	0.073	0.019
butane	0.000	0.033	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,3-butadien	0.01	0.006	0.010	0.006	0.004	0.006	0.008	0.016	0.005	0.008	0.016	0.005
propane	0.00	0.004	0.003	0.000	0.001	0.003	0.004	0.007	0.002	0.004	0.007	0.002

1-buten-3-in	0.00	0.002	0.003	0.006	0.001	0.003	0.004	0.007	0.002	0.004	0.007	0.002
cyklopentadien	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
benzene	0.02	0.051	0.089	0.051	0.036	0.051	0.006	0.006	0.002	0.006	0.006	0.002
toluene	0.01	0.011	0.017	0.011	0.008	0.011	0.001	0.000	0.000	0.001	0.000	0.000
suma	100.0	100.00	100.00	100.00	100.00	100.00	100.1	100.1	100.1	100.0	100.0	100.0
LHV,MJ/m3	3.62	3.521	4.164	3.521	2.780	3.521	3.521	4.387	5.009	3.541	3.005	5.009

Table 12.2 Gas composition pre and post active carbon filter

Other gas components denoted as C_XH_Y pre and post the active carbon filter recorded as shown in Fig.12.7 .The amounts of Ar, Ethan and Ethylene were almost around the same level however other components slightly decreased and some were completely disappeared.

The low heating value of the resultant gas obtained was in an acceptable level that it reached 5MJ/m^3 which is possible to consider as a successful method for gas cleaning since the normal LHV of the producer gas is 4 - 7 MJ/m^3_n and the acceptable value of solid particles (soot, dust and ash) is 1.5 g/m^3_n calculated at T=0°C and P=101 kPa, where it is very possible for any cleaning process to result a sudden drop in LHV value.

Fig 12.8 shows the resultant LHV pre and post the active carbon filter.

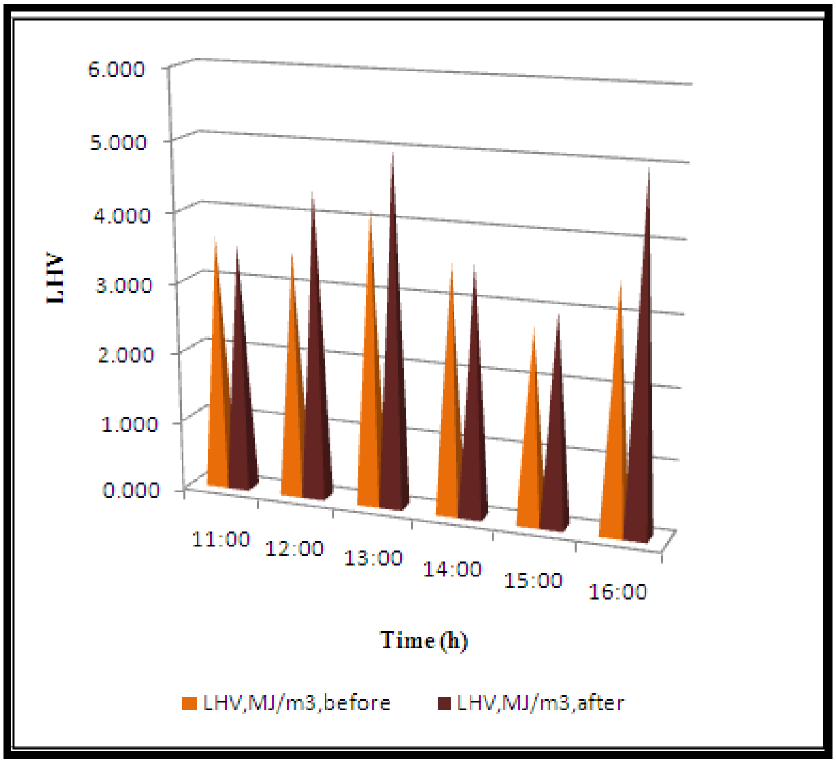


Figure 12.8 LHV (MJ/m^3) pre and post active carbon filter

12.2 Tar samples analysis

Tar samples analysis using the active carbon material show a significant success due to the impressive results which indicates the capability of this material for tar cracking during biomass gasification process. The percentage of cracking for almost all the classified tar components where the amounts and the concentration have been deducted almost zero. These results applied to heterocyclic aromatics - Class II like pyridine, phenol, cresol, and quinoline, Class III - aromatics (1 ring) like xylene, styrene and toluene, light PAH (2, 3 ring) - Class IV like naphthalene; methyl-naphthalene; biphenyl; ethenylnaphtalene; Acenaphthylene; acenaphtene; fluorene; Phenanthrene and anthracene as well as the heavy PAH (>3 rings) like fluoranthen; Pyrene; benzo-anthracene; chrysene; benzo-fluoranthene; benzo-Pyrene; perylene; Indeno-pyrene; Dibenzo-anthracene and Benzo-perylene. Table 12.3 illustrates the amount and concentration pre and post the active carbon filter.

Class II	**Component**	**Pre filter**	**Post filter**	
		Concentration mg/m^3	**Concentration mg/m^3**	**Tar removal efficiency %**
	Phenol	147.0	0	100%
	Methyl phenol	0,0	0	100%
	Benzofuran		0	100%
	Dibenzofuran	60.9	0	100%
	Methylbenzofuran	4.1	0	100%
	Naphtha Benzofuran	0.0	0	100%
Class IV	**Component**	**Pre filter**	**Post filter**	
		Concentration mg/m^3	**Concentration mg/m^3**	**Tar removal efficiency %**
	Methylnaphthalene	72.9	0	100%
	Biphenyl	29.2	0	100%
	Acenaphthylene	93.3	0	100%
	Fluorene	27.2	0	100%
	Phenanthrene	23.2	0	100%
	Methylphenantren	0.8	0	100%
Class V	**Component**	**Pre filter**	**Post filter**	
		Concentration mg/m^3	**Concentration mg/m^3**	**Tar removal efficiency %**
	Fluoranthen	2.3	0	100%
	Pyrene	4.4	0	100%
	Methyl fluoranthen	0.0	0	100%
	Methylpyrene	0.0	0	100%
	Anthracene	8.0	0	100%
	Fluorene	2.3	0	100%

Table 12.3 Tar composition and tar removal efficiency % pre and post filter

Analysis results show that most the tar components in spite of classes were completely adsorbed within the active carbon material filter.

It was found that even the concentration of Benzene and Toluene has been decreased to recognizable values this is shown in Fig. 12.9.

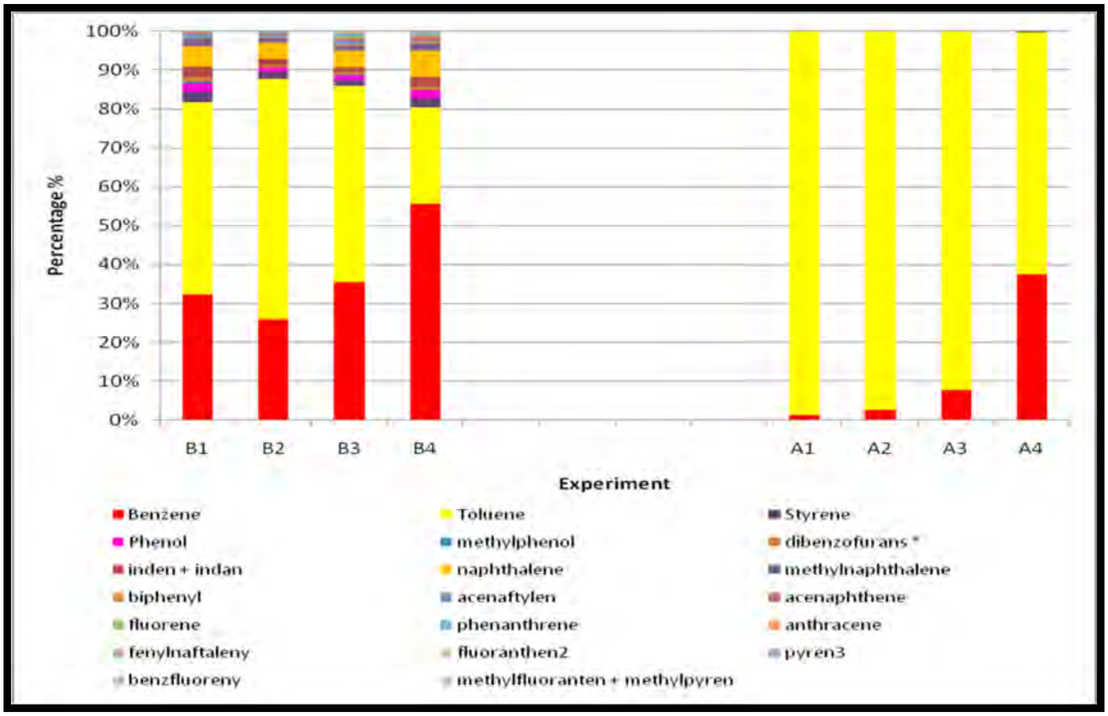


Figure 12.9 Tar components per unit volume pre and post active carbon filter

Fig.12.10 shows the concentration percentage of each tar component pre and post the active carbon filter without Benzene.

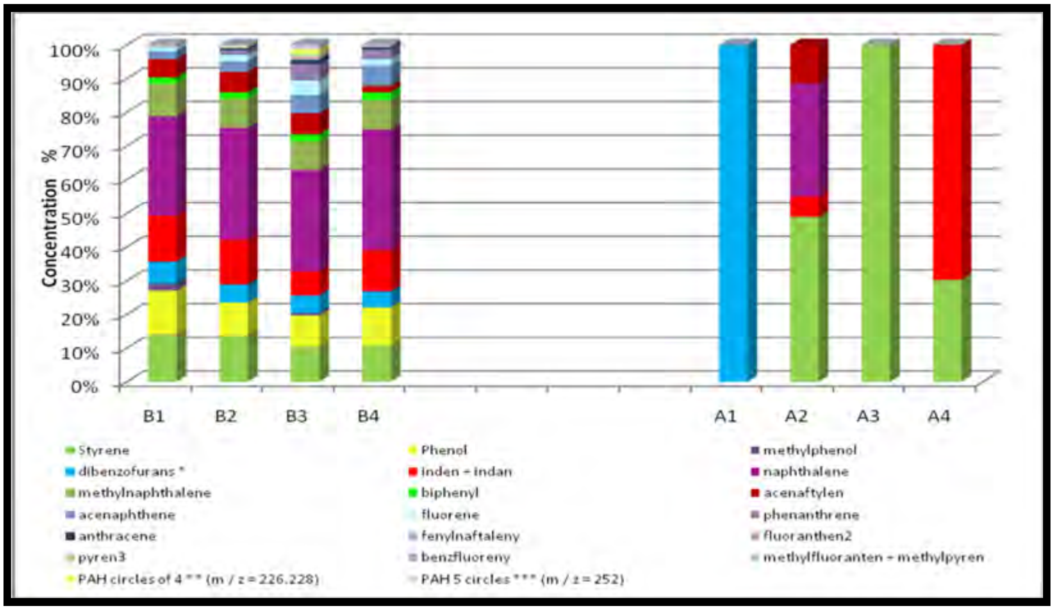


Figure 12.10 Tar components per unit volume pre and post active carbon filter without Benzene

The tar removal using active carbon material in temperatur ranges between 70 - 200 °C was completly sucsseful for different PAH 4,5,6 circles that it is possible to confirm 100% efficiency. This sucsses encouraged to continue the experimental work to get a new series of data by examinining different range of temperatures and different amount of active carbon material.

Average tar concentration analysis for the three experiments pre and post the active carbon filter is illustrated in Table 12.4.

Description / start collecting	11:40-12:20	12:45-13:15	12:25-14:50	15:25-16:00	11:40-12:30	12:45-13:15	14:25-14:50	15:15-16:00
sample (marked)	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008
volume of gas, l	98.0	95.0	100.0	71.0	103.0	132.0	120.0	150.0
Volume of acetone, ml	150	151	149	174	161	145	164	130
date	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008	29.04.2008
taking place:	**Before**	**Before**	**Before**	**Before**	**After**	**After**	**After**	**After**
Benzene	3561	3226	1355	4555	108	131	72	96
Toluene	5473	7685	1921	2051	9209	4978	856	160
m + p + o-xylene + ethyl benzene + phenylethyn	124	101	51	126	8	2	2	1
Styrene	288	213	57	171	0	1	0	0
C3-benzene summa (nas + NENAs)	211	162	3	74	1	2	0	1
others 1	0	45	1	0	0	50	4	0
BTX summa	9658	11433	3390	6978	9326	5165	933	257
oxygen summa	433	231	86	258	1	0	0	0
Phenol	259	147	52	182	0	0	0	0
Mathylphenol	44	0	4	0	0	0	0	0
Dibenzofuran *	131	82	28	76	1	0	0	0
Nitrogen	0	2	1	0	0	0	0	0
inden + indane	277	204	40	197	0	0	0	0
naphthalene	596	508	167	573	0	1	0	0
methylnaphthalene	194	132	46	139	0	0	0	0
ALKYLNAPHTHALENES (Alkyl> = C2)	66	52	25	59	0	0	0	0
biphenyl	38	29	12	37	0	0	0	0
Acenaphthylene	111	93	34	30	0	0	0	0
acenaphtene	49	48	30	97	0	0	0	0
fluorene	25	27	24	30	0	0	0	0
PAH o M / Z = 165.166	18	14	17	16	0	0	0	0
Phenanthrene	2	23	27	45	0	0	0	0
anthracene	2	8	7	12	0	0	0	0
methylfenantren 4 H-cyclopenta [def] Phenanthrene	1	6	7	12	0	0	0	0
fenylnaftaleny	0	1	1	3	0	0	0	0

fluoranthen2	1	3	4	4	0	0	0	0
pyren3	2	4	4	4	0	0	0	0
benzfluoreny	0	0	1	0	0	0	0	0
methylfluoranten + Methylpyrene	0	0	0	0	0	0	0	0
PAH circles of 4 ** (m / z = 226.228)	2	3	8	0	0	0	0	0
PAH 5 circles * (m / z = 252)**	3	4	7	0	0	0	0	0
summa tar (non-BTX)	1887.1	1440.0	571.1	1565.6	1.6	1.3	0.0	0.3

Table 12.4 Tar analysis (average) pre and post the active carbon filter

12.3 Second series of active carbon filter experiments – Results and discussion

Examining the active carbon filter in a new series of experements was ramarkable in order to study the ability of this materile to handle the different ranges of temperature using only 200ml of active carbon material. This will enable to study both inflouance of temperature and amount on tar cracking. Table 12.5 shows the experimental conditions for the second series of experiments.

Experimental conditions	Exp.no.1	Exp.no.2	Exp.no.3	Exp.no.4
Temperature of the active carbon filter	70 ° C	100 ° C	150° C	200° C
Active carbon sample weight	50g	50g	50 g	50 g
Active carbon particle size	0.2 mm	0.2 mm	0.2 mm	0.2 mm
Gas flow rate through the hot catalytic filter during sampling	5 lit/sec	5 lit/sec	5 lit/sec	5 lit/sec
Amount of gas for tar sampling	100 lit	100 lit	100 lit	100 lit

Table 12.5 Experimental conditions of the second series of experiments with active carbon filter

Six experiments has been done in different six temperatures starting from 70° C - 200°C, it was found that all tar components of classes II, IV and V are entirely adsorbed by the active carbon material with a percentage of 100% as shown in Table 12.6 shows tar classes' concentration pre and post active carbon filter.

Date:	28/04/2009	28/04/20092	28/04/20093	28/04/20094	28/04/20095	28/04/20096	28/04/20097	28/04/20098	28/04/20099	28/04/200910	28/04/200911	28/04/200912
Amount of Acetone, ml	80	150	220	132	100	110	133	116	124	113	115	120
Place of sample:	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
Class 2	378	306	187	199	115	297	1	0	1	0	0	0
Class 4	1526	2015	1726	984	1255	1637	0	1	1	0	0	1
Class 5	17	9	18	27	22	13	0	0	0	0	0	0
Sum of Tar (without BTX)	1921.0	2330.0	1931.0	1210.0	1392.0	1947.0	1.0	1.0	2.0	0.0	0.0	1.0
BTX sum - Class 3	7856	9567	6891	10258	8754	9647	7645	6108	5201	7832	6230	5405

A=after the filter B=before the filter

Table 12.6 Tar classes (average) concentration pre and post active carbon filter

The temperature distribution inside the active carbon filter during the experiment shown in Fig. 12.11.

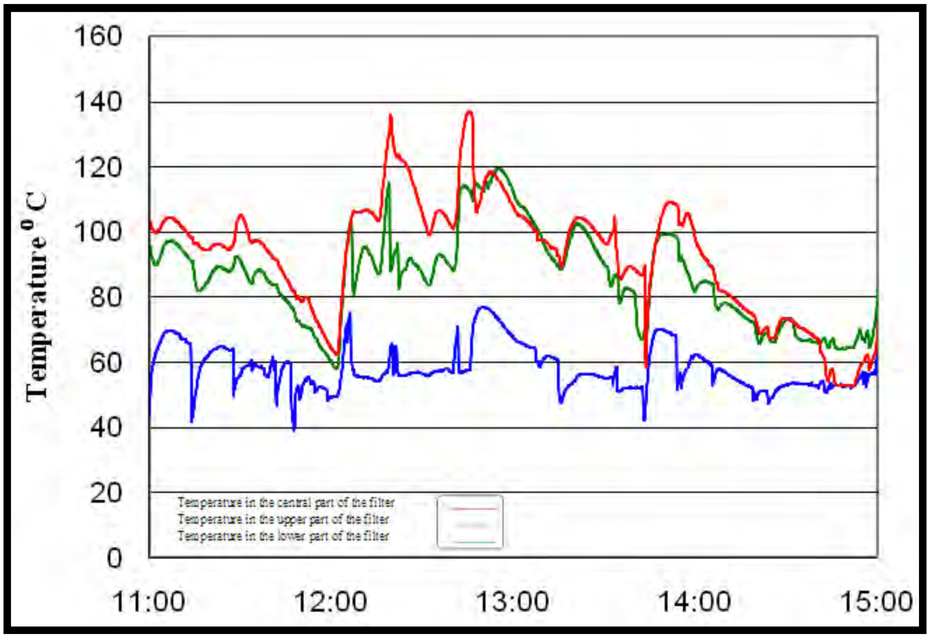


Figure 12.11 Temperature distributions inside the active carbon filter

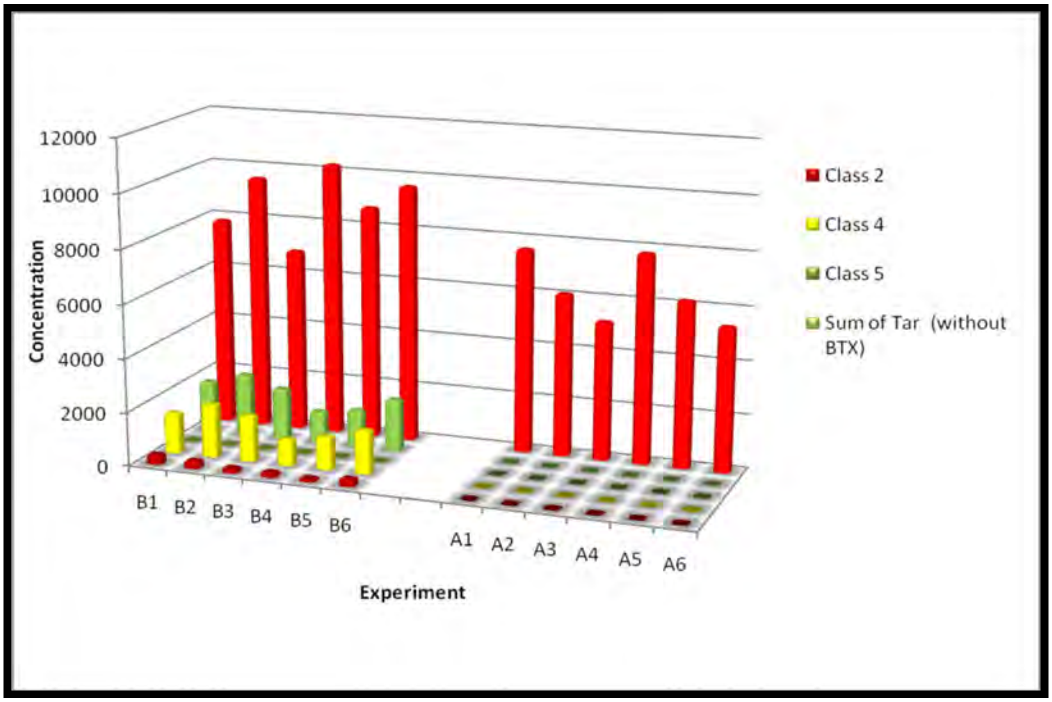


Figure 12.12 Concentration of tar per unit volume pre and post the active carbon filter

Fig.12.12 shows the concentration of the different tar classes' pre and post the active carbon filter. It is shown that the class III of tar components is the only component remained in the samples with lower concentration where the others were disappeared.

12.4 Third series of active carbon material filter experiments – Results and discussion

In order to study the period for the active carbon filter to reach the saturation, 'the time for the material to loss it's ability to absorpe an extra amounts of tat components as a result of pores blockage, a series of experermints were achieved using 200ml of active carbon in a sereies of different temperature experemts. It was found that there was no signs of pores blockage on the resultant data obtained which supported the idea of the utilization of active carbon material as a strong candidate for tar cracking in biomass gasification

Date:	06/05/2009	06/05/2009	06/05/2009	06/05/2009	06/05/2009	06/05/2009	06/05/2009	06/05/2009
Amount of Acetone, ml	176	110	121	155	100	100	100	150
Place of samples:	**B1**	**B2**	**B3**	**B4**	**A1**	**A2**	**A3**	**A4**
Class 2	305	387	298	277	8	12	4	9
Class 4	1926	1896	1356	1785	7	6	6	12
Class 5	31	12	16	29	0	0	1	1
sum of Tar (without BTX)	2262.0	2295.0	1670.0	2091.0	15.0	18.0	11.0	22.0
BTX sum - Class 3	8207	9113	5452	6707	6421	6847	4703	4923

A= After B= Before

Table 12.7 Concentration (Average) of different tar classes pre and post the active carbon filter

The results obtained showed that the tar components of classes II, IV and V were completely adsorbed by the active carbon material where the class III components remained in lower concentration. These results obtained in repeated use are almost the same as the results obtained after the utilization of the active carbon filter for the first time which means that the active carbon material has the ability to handle enough a mounts after a multiple use. This particularity has a massive importance in the industrial utilization of the active carbon material in the purification of gas produced from biomass gasification especially if the resident time of this material has been studied.

Table 12.8 shows the efficiency of the active carbon material in different range of temperatures.

Fig. 12.13 shows the tar classes' concentration pre and post active carbon filter. It is clearly shown that big differences achieved pre and post this material.

Gasification Temperature 800-850 °C						
Filter Temperature	70°C	90°C	100°C	130°C	150°C	200°C
Efficiency of 400 ml	95%	96%	97%	98%	97%	96%
Efficiency of 200 ml	96%	96%	97%	98%	97%	96%

Table 12.8 Efficiency of different amounts of active carbon material during the experiments As a function of filter temperature

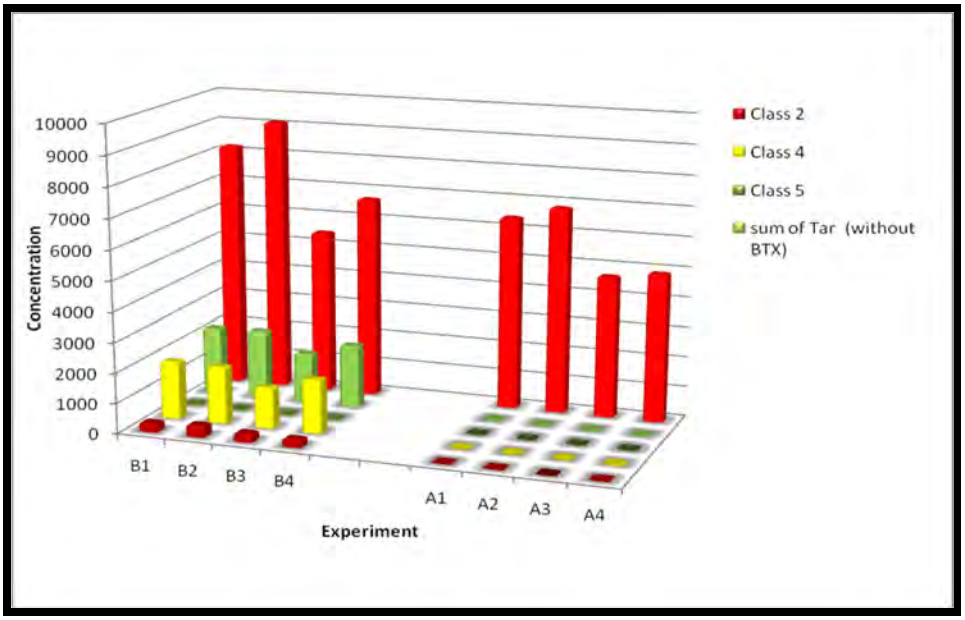


Figure 12.13 Tar classes' concentration per unit volume pre and post active carbon filter

12.5 Specifications of active carbon material after multiple utilization

Active carbon material is a pores material features with a huge serfacr area and the utilization of this material for tar cracking in biomass gasification depends mainly on the ability of this material to adsorp the different high density PAH components taking in account that the multiple utilization may cause theses components may couse blockage of active carbon pores. It was found that there is no change in color, size, hardness or physical properties of the material after multiple uses. It is very possible to reactivate and reuse this material since it will present a practical solution involves an economical purpose for gas purification.

Fig. 12.14 shows the active carbon material pre and posts multiple uses in the experiments.

Figure 12.14 Active carbon material pre and posts multiple uses in the experiments

13. Conclusions

[1] The utilization of biomass feed stocks and wooden residue for gasification process to produce syngas suitable for the implementation of power plants of electricity generation.

[2] Since the obtained gas has many types of unwanted contaminants. It was necessary to derive an effective cleaning method for gas purification from Dust, Chemical contaminants and tar components.

[3] Three kinds of carbon materials has been use successfully and efficiently, char coal, black coke and active carbon. The three materials gave different results.

[4] Char coal material gave acceptable results in both gas and tar components purification, thanks to its fragile nature and the huge surface area due to porous of this material.

[5] Black coke material is an inefficient material for tar cracking however it has a good ability for gas contaminants adsorption.

[6] Active carbon is the best material tasted in a range of temperatures and a series of efficient experiments. This material gave the desired results which encouraged working further in order to investigate the maximum ability of this material either for tar cracking in another temperature series or the saturation degree suitable to be known for the industrial purposes. Fig 13.1 shows the efficiency of 400ml of each carbon material verses the filter temperature.

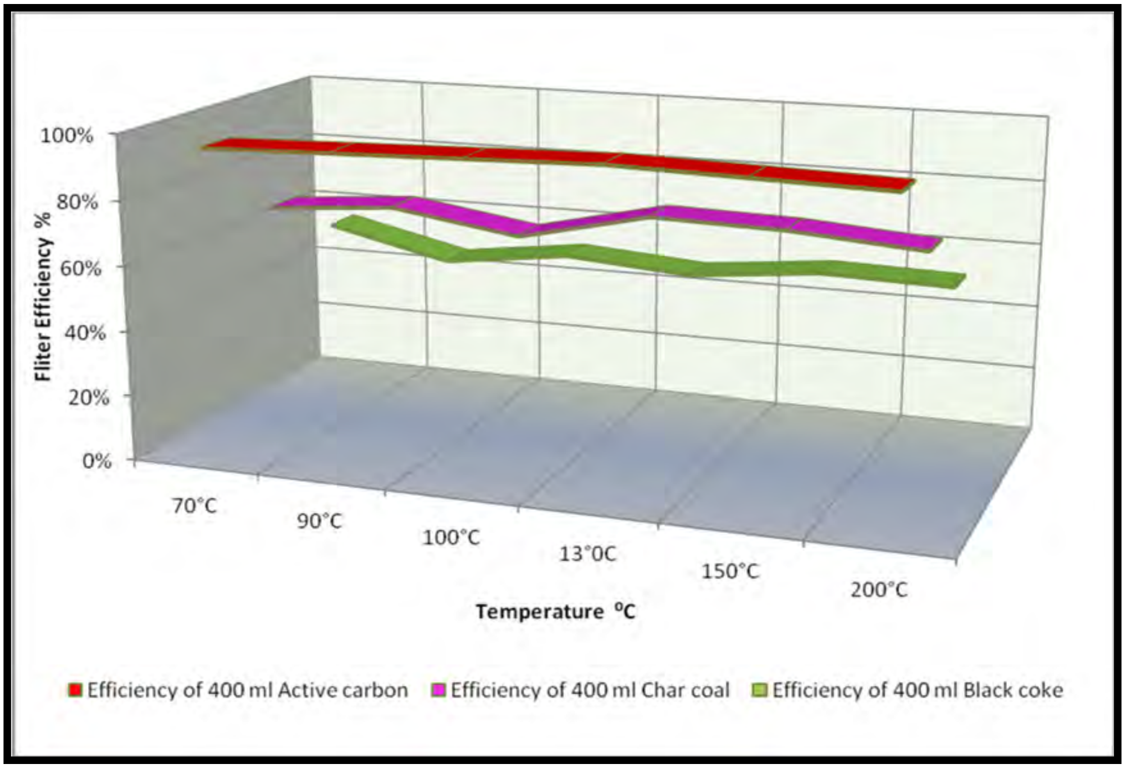


Figure 13.1 Carbon filter efficiency as a function of filter temperature

The maximum efficiency achieved was using the active carbon material with the amount of 400ml at the temperature of 110^{o}C where the maximum efficiency of the 200ml of active carbon material was at the temperature of 100^{o}C as shown in Fig.13.2.

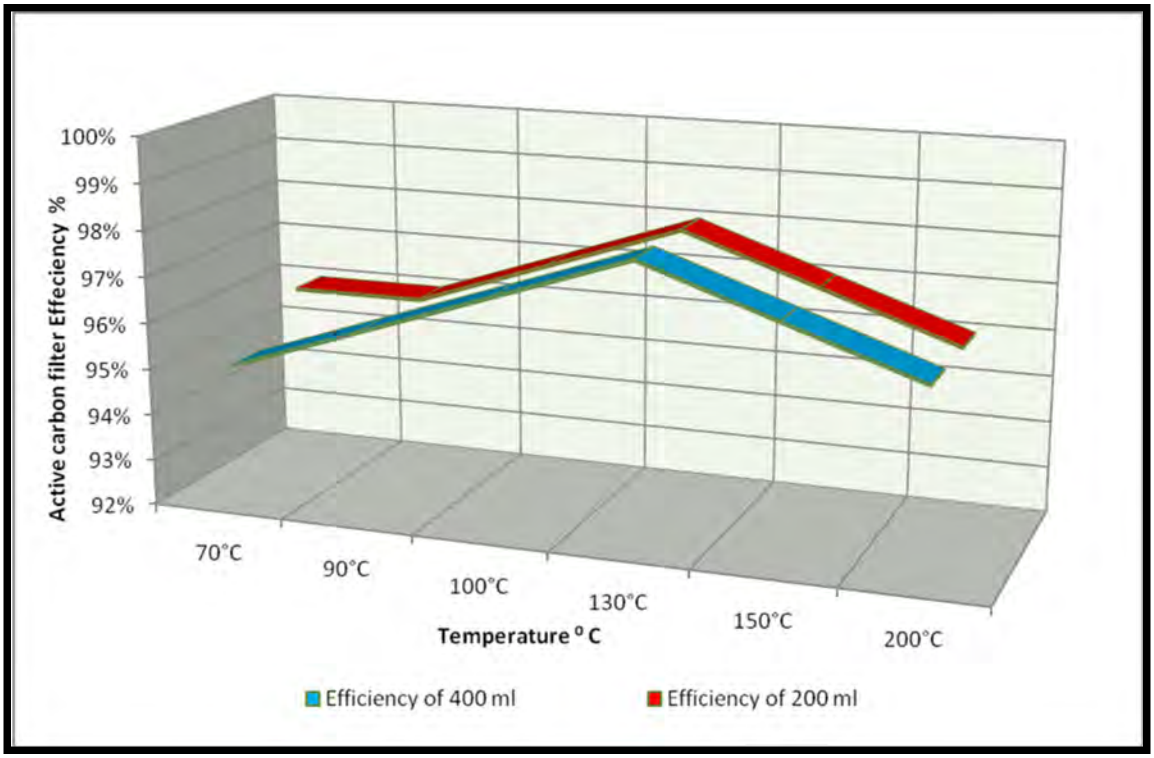


Figure 13.2 Active Carbon filter efficiency as a function of filter temperature

14. Evaluation of experimental and theoretical results

Since the carbon materials adsorption are following the BET Theory put forward by Brunauer, Emmett and Teller explained that multilayer formation which is the true picture of physical adsorption and the Freundlich Adsorption Isotherm which is mathematically expressed as:

$\frac{x}{m} - Kp^{1/n}$ Or: $\frac{x}{m} - Kc^{1/n}$

Where:

x = mass of adsorbate

m = mass of adsorbent

p = Equilibrium pressure of adsorbate

c = Equilibrium concentration of adsorbate in solution.

K and $1/n$ are constants for a given adsorbate and adsorbent at a particular temperature.

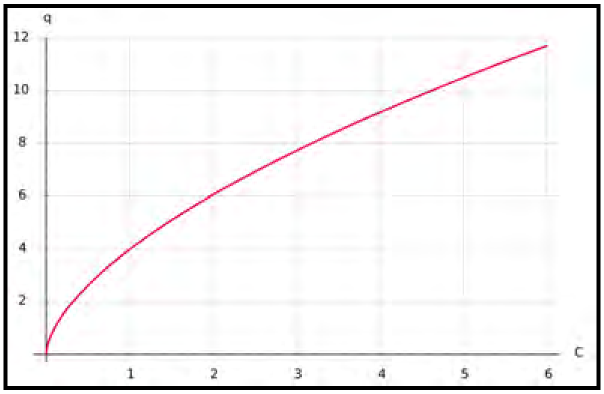


Figure 13.3 Freundlich Adsorption Isotherm

The theory is a rule of the physical adsorption of gas molecules and serves the basis for an important analysis technique for measurement of specific surface area of a material. Under the conditions of high pressure and low temperature, thermal energy of gaseous and would be available per unit service area. The activated carbon adsorption capacity parameters and properties can be described as:

- **Capacity parameters:** determine loading characteristics of activated carbon. Maximum adsorption capacity of activated carbon is only achieved at equilibrium.

- **Kinetic parameters:** determine the rate of adsorption and have negligible effect on adsorption capacity.

  - Surface Area**:** Adsorption capacity is proportional to surface area (determined by degree of activation).

  - Pore Size**:** Correct pore size distribution is necessary to facilitate the adsorption process by providing adsorption sites and the appropriate channels to transport the adsorbate.

  - Particle Size: Smaller particles provide quicker rates of adsorption.

Note: Total surface area is determined by degree of activation and pore structure and not particle size.

  - Temperature**:** Lower temperatures increase adsorption capacity except in the case of viscous liquids.

  - Concentration of Adsorbate**:** Adsorption capacity is proportional to concentration of adsorbate.

- pH**:** Adsorption capacity increases under pH conditions, which decrease the solubility of the adsorbate (normally lower pH).

- Contact Time**:** Sufficient contact time is required to reach adsorption equilibrium and to maximize adsorption efficiency.

15. Suggestions for future work

[1] Testing the resident life time for the active carbon material to investigate the efficiency of this material for very frequent utilization.
[2] Modeling of the equipment for industrial work is very possible due to the successful results obtained and the simplicity of both design and experimental procedure.
[3] The utilization of carbon materials frequently for gas purification in industrial plants will be no longer expensive because of the ability of either reactivation or using the saturated material as a feed stock during the gasification process. This will support the procedure economically.
[4] Resize the filter to fit the industrial requirements and or increase the filter dimensions in order to fit further amounts of carbon material if this will help according to the industrial requirements.
[5] To reach the optimal design it is possible to change the gas inlets and outlets if it is necessary to obtain the perfect performance.
[6] Improve the design using two or three stages of carbon material filters to reach the acceptable levels suitable with different industrial requirements.

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List of symbols

$C_{ash,fuel}$	Ash content of fuel [kg / kg dry biomass]
F*m*	Weight fraction of moisture produced in combusted gases
h*w*	Heat of vaporization of water (2257 kJ kg^{-1})
Q_i	MJ/m^3
Q_s	MJ/m^3
r	Contents of water in the fuel
V	Volume of gas adsorbed at equilibrium (m^3)
P	Gas equilibrium pressure (kPa)
V (P)	Predicated amount of gas adsorbed at P
V_L	Langmuir volume parameter (m^3)
P_L	Langmuir pressure parameter (m^3)
θ	Number of sites of the surface
K	The equilibrium constant for distribution of adsorbate
P^*	Saturation pressure (kPa)
R	Gas constant J/K mol
Δ_{vap} H	Enthalpy of vaporization (J)
Δ_{des} H	Enthalpy of desorption (J)
V_{mono}	The adsorbed volume of gas at high pressure (m^3)
ΔG_0	Gibb's free energy (kJ/mol)
ΔH_R	The heat of reaction
$\Delta\ H_c$	The heat of combustion of species
n_i	The moles of species
Cpi	The specific heat capacity of species (J/K).
$q_{m,fuel}$	Fuel feeding rate [kg dry biomass / h]
CC_{fuel}	Carbon content of fuel [kg C / kg dry biomass]
$q_{v,agent}$	Gasification agent feeding rate [m^3n/h]
CC_{agent}	Carbon content of gasification agent [kg C / m^3n]
$q_{v,gas}$	Producer gas generation rate [m^3n/h]
CC_{gas}	Carbon content of non – condensable gases
C_{tar}	Tar concentration in producer gas [kg C / m^3n]
CC_{tar}	Carbon content of tar [kg C / kg tar]
$C_{particles}$	Particles concentration in producer gas [kg C / m^3n]
$CC_{particles}$	Carbon content of particles [kg C / kg dry biomass]
$q_{m,ash}$	Bottom ash rate [kg dry ash / h]
CC_{ash}	Carbon content of bottom ash [kg C / kg dry ash]
Y_{gas}	Producer gas yield [m^3_n/ kg dry biomass]
x	Mass of adsorbate (Kg)
m	Mass of adsorbent (Kg)
p	Equilibrium pressure of adsorbate
c	Equilibrium concentration of adsorbate in solution.

Author’s Publications

1. KADAM, S.: A review of Tar from biomass product gas and Tar removal Technologies, Proceeding of (Summaries 4, PRES 2008 and System Engineering, pp.1602-16011, (2008), The 18th International Congress of Chemical and Process Engineering CHISA 2008, Prague Czech Republic, A conference paper. 18th International Congress of Chemical and process Engineering Chisa 2008, Paha, 24.08.2008-28.08.2008

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3. KADAM, S.S.: An experimental study to improve Tar Removal in Biomass Gasification, Proceeding of (Energie Z Biomasy IX, Sbornik přespěvku ze seminaře, pp111-118 (2008), ISBN: 978-80-214-3803-3, Seminar paper, Energie Z Biomasy IX, 18th -19th Nov. 2008 Brno.

4.AL-DURY S.S.K.: Removal of tar in Biomass Gasification Process using carbon materials, Proceeding of (Part 2, Pres’09, pp.665-670, (2009), PRES’09 Roma – Italy, Conference paper, 12th International conference on Process Integration, and Modeling and Optimization for Energy Saving and Pollution Reduction. 10th -13th May 2009 Rome- Italy.

5. AL-DURY S.S.K.: Biomass Product Gas, Typical contaminants, Clean up and removal Technologies, VP2.2.6. 17th European Biomass Conference and Exhibition in Hamburg - Germany 29th June -3rd July 2009.

6.AL-DURY S.S.K.: Pollutants Removal from Syngas using Carbon Materials, IASTED International Conference on Environmental Management and Engineering ~EME 2009~ July 6 – 8, 2009 Banff, Alberta, Canada, Proceeding (650), (650-046) ISBN (CD): 978-0-88986-797-0

7. AL-DURY S.S.K.: Tar formation in biomass gasification, 8th World Congress of Chemical Engineering - Montreal – Canada, August 23 to 27, 2009, Proceeding 00000070 Al - Dury, S., WCCE8 - ISBN 0-920804-44-6.

8. AL-DURY S.S.K.: Improvement of gas cleaning in biomass gasification, comparison study, 8th World Congress of Chemical Engineering, Montreal – Canada, August 23 to 27, 2009, Proceeding 00000071 Al - Dury, S., WCCE8 - ISBN 0-920804-44-6.

9.AL-DURY S.S.K.: The utilization of activated carbon for gas cleaning in biomass gasification process, 8th World Congress of Chemical Engineering, Montreal – Canada, August 23 to 27, 2009 ,Proceeding 00000073, Al - Dury, S. WCCE8 - ISBN 0-920804-44-6.

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