

**TAR REMOVAL FROM PRODUCER GAS VIA
THERMAL AND CATALYTIC MEANS IN A
MICROWAVE REACTOR**

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CATALYTIC MEANS IN A MICROWAVE REACTOR**

by

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LIST OF ABBREVIATIONS

1-MN	1-Methylnaphthalene
Al	Aluminium
Al ₂ O ₃	Alumina
Ar	Argon
C	Carbon
C ₂ H _x	Hydrocarbons with two carbon atom
C ₆ H ₆	Benzene
C ₇ H ₈	Toluene
C ₈ H ₁₀	Xylene
C ₁₀ H ₈	Naphthalene
Ca	Calcium
CaO	Calcium Oxide (Calcite)
Ce	Cerium
CeO ₂	Ceria
CH ₄	Methane
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
C _n H _m	Representing hydrocarbons lower than tar compounds
Cs	Cesium
C _x H _y	Representing tar compounds
DTG	Differential Thermogravimetric
EFB	Empty Fruit Bunch
ER	Equivalence Ratio

FCC	Fluid Catalytic Cracking
FEPA	Federation of European Producers of Abrasives
FICFB	Fast Internally Circulating Fluidized-bed Gasifier
Fr	Francium
GC	Gas Chromatography
H ₂	Hydrogen
H ₂ O	Water or steam
HACA	Hydrogen Abstraction Carbon Addition
He	Helium
HHV _b	Higher Heating Value of Biomass (MJ kg ⁻¹)
HHV _{PG}	Higher Heating Value of Producer Gas (MJ Nm ⁻³)
HPAH	Heavy Poly-Aromatic Hydrocarbon
IC	Internal Combustion
IGCC	Integrated Biomass Gasification and Combined Cycle
K	Potassium
LAH	Light Aromatic Hydrocarbon
LHV	Lower Heating Value (MJ Nm ⁻³)
LHV _b	Lower Heating Value of Biomass (MJ kg ⁻¹)
LHV _{PG}	Lower Heating Value of Producer Gas (MJ Nm ⁻³)
Li	Lithium
LPAH	Light Poly-Aromatic Hydrocarbon
LPG	Liquefied Petroleum Gas
Mg	Magnesium
MgO	Magnesium Oxide (Magnesite)
MGT	Model Gas Tar

Mo	Molybdenum
MS	Mass Spectrophotometry
N ₂	Nitrogen
Na	Sodium
NO _x	Nitrogen Oxide
Ni	Nickel
NiO	Nickel Oxide
O ₂	Oxygen
PAH	Poly-Aromatic Hydrocarbon
Pd	Palladium
PGT	Producer Gas Tar
PID	Proportional band, Integral and Derivative time action
Pt	Platinum
Rb	Rubidium
Rh	Rhodium
Ru	Ruthenium
SEE	Standard Error of the Estimate
SiC	Silicon Carbide
SiO ₂	Silica
SO ₂	Sulfur Dioxide
TCD	Thermal Conductivity Detector
TGA	Thermogravimetric Analyzer
TiO ₂	Titania
TWT	Traveling Wave Tube
VOC	Volatile Organic Compound

Z β	β -Zeolite
ZrO ₂	Zirconia
ZY	Y-Zeolite
LZY	Linde Y-Zeolite

LIST OF SYMBOLS

A	Reactor cross sectional area (m^2)
B	Mass balance closure (%)
c_p	Heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
C_{fp}	Fine particulates concentration (g Nm^{-3})
C_i	Concentration of reactant species (g Nm^{-3})
C_{in}	Inlet tar concentration (g Nm^{-3})
C_{out}	Outlet tar concentration (g Nm^{-3})
C_T	Tar concentration (g Nm^{-3})
C_w	Water concentration (g Nm^{-3})
d_T	Total diameter of the insulation reactor (m)
D_p	Penetration depth of microwave power (m)
E	Activation energy (kJ mol^{-1})
E_{rms}	Electric field (V m^{-1})
f	Frequency (Hz)
$F_{exp,i}$	Yields of products obtained by experimental
$F_{mod,i}$	Yields of products estimated by the kinetic model
F_H	Amount of hydrogen (g)
F_O	Amount of organic hydrocarbons (g)
F_S	Amount of coke/soot (g)
F_T	Mass of the remaining condensed tar (g)
$F_{T,0}$	Initial mass of tar model (g)
\dot{F}_{fp}	Mass input/output of fine particulates (kg h^{-1})

\dot{F}_{PG}	Producer gas mass flow rate (kg h ⁻¹)
\dot{F}_S	Mass input/output of soot (kg h ⁻¹)
\dot{F}_T	Mass input/output of tar (kg h ⁻¹)
\dot{F}_w	Mass input/output of water (kg h ⁻¹)
h_i	Convective heat transfer coefficient inside the reactor (W m ⁻² K ⁻¹)
h_o	Convective heat transfer coefficient outside the reactor (W m ⁻² K ⁻¹)
H	Energy balance closure (%)
$H_{c(fp)}$	Heat of combustion of particulates (MJ h ⁻¹)
$H_{c(PG)}$	Chemical energy of the clean dry producer gas (MJ h ⁻¹)
$H_{c(S)}$	Heat of combustion of coke (MJ h ⁻¹)
$H_{c(T)}$	Heat of combustion of tar (MJ h ⁻¹)
H_{fp}	Energy in fine particulates (MJ h ⁻¹)
H_i	Total energy input (MJ h ⁻¹)
H_o	Total energy output (MJ h ⁻¹)
H_{PG}	Energy in producer gas (MJ h ⁻¹)
H_S	Energy in coke (MJ h ⁻¹)
H_T	Energy in tar (MJ h ⁻¹)
H_w	Energy in water (MJ h ⁻¹)
$H_{w(vapor)}$	Energy in water in vapor state (MJ h ⁻¹)
ΔH_{fp}	Sensible heat of particulates (MJ h ⁻¹)
ΔH_{PG}	Sensible heat of the clean dry producer gas (MJ h ⁻¹)
ΔH_S	Sensible heat of coke (MJ h ⁻¹)
ΔH_T	Sensible heat of tar (MJ h ⁻¹)
ΔH_w	Sensible heat of water (MJ h ⁻¹)
k	Kinetic rate constant (s ⁻¹)

k_0	Pre-exponential/frequency factor (s^{-1}) or ($m^3 kg^{-1} h^{-1}$)
$k_{insulation}$	Thermal conductivity of the insulation material ($W m^{-1} K^{-1}$)
k_{pipe}	Thermal conductivity of the reactor material ($W m^{-1} K^{-1}$)
L_i	Height of the reactor at zone i (m)
\dot{m}_b	Mass flow rate of the biomass fuel ($kg h^{-1}$)
M_i	Total mass input ($kg h^{-1}$)
M_o	Total mass output ($kg h^{-1}$)
MW_{PG}	Dry molecular weight of producer gas ($kg kmol^{-1}$)
n	Sample number
P	Pressure of producer gas at the outlet of tar sampling train (kPa)
P_{abs}	Absorbed microwave power (W)
P_{MW}	Output power of the microwave oven (W)
P_o	Incident microwave power at the material surface (W)
$P(z)$	Microwave power at distance z (W)
Q	Gas flow rate ($m^3 h^{-1}$)
Q_{cond}	Heat conduction (W)
Q_{conv}	Heat convection (W)
Q_{PG}	Volumetric flow rate of the producer gas ($Nm^3 h^{-1}$)
Q_{rad}	Heat radiation (W)
r_H	Formation rate of hydrogen ($g Nm^{-3} s^{-1}$) or ($g s^{-1}$)
r_O	Formation rate of organic hydrocarbons ($g Nm^{-3} s^{-1}$) or ($g s^{-1}$)
r_S	Formation rate of coke/soot ($g Nm^{-3} s^{-1}$) or ($g s^{-1}$)
r_T	Conversion rate of tar ($g Nm^{-3} s^{-1}$) or ($g s^{-1}$)
R	Universal gas constant ($0.008314 kJ mol^{-1} K^{-1}$)
R_I	Inner radius of the reactor (m)

R_2	Outer radius of the reactor (m)
R_3	Outside radius of the insulation reactor (m)
t	Time period (s)
$\tan \delta$	Loss tangent
T	Reaction temperature (K)
$T_{ambient}$	Ambient or surrounding temperature (K)
T_e	Average temperature at the outlet of tar sampling train (K)
T_{inlet}	Reactor inlet temperature (K)
T_o	Reactor outer surface temperature (K)
T_R	Residence time (s) or (kg h m ⁻³)
\bar{T}	Average temperature within the reactor (K)
U	Overall heat transfer coefficient (W m ⁻² K ⁻¹)
V	Volume of absorber material (m ³)
V_{eff}	Effective bed reaction volume with respect to the volume of empty reactor (m ³)
W_c	Amount of catalyst loading (kg)
x_{CH_4}	Volume fraction of methane
x_{CO}	Volume fraction of carbon monoxide
x_{H_2}	Volume fraction of hydrogen
X_H	Mass fraction of hydrogen
X_O	Mass fraction of organic hydrocarbons
X_S	Mass fraction of coke/soot
X_T	Tar conversion
α	Coke/soot reduction activity constant (s ⁻¹)
α_0	Pre-exponential factor of soot reduction activity (s ⁻¹) or (m ³ kg ⁻¹ h ⁻¹)

β	Maximum theoretical soot yield
ε	Emissivity of material
ε'	Dielectric constant
ε''	Dielectric loss factor
ε^*	Complex dielectric constant
ε_0	Permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$)
γ	Maximum theoretical organic hydrocarbons yield
Γ	Soot reduction activity function
κ	Attenuation constant
ρ	Density (kg m^{-3})
σ	Stefan-Boltzman constant ($5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$)
η_{cg}	Cold gas efficiency (%)
η_P	Absorption power efficiency (%)
λ_0	Free space wavelength of the microwave radiation (12.23 cm)
ϕ	Thiele modulus

PENYINGKIRAN TAR DARI GAS PENGELUAR MELALUI CARA TERMAL DAN PEMANGKIN DALAM REAKTOR GELOMBANG MIKRO

ABSTRAK

Tar dalam gas pengeluar biojisim perlu disingkirkan untuk mengelak saluran paip tersekat dan untuk membolehkan penggunaan gas pengeluar dalam enjin pembakaran dalam (IC) dan turbin untuk penjanaan kuasa. Antara kaedah penyingkiran tar yang sedia ada, rawatan tar terma dan pemangkin (hababermangkin) adalah lebih menarik dengan peningkatan kandungan tenaga gas pengeluar di mana tar ditukarkan kepada gas boleh bakar. Walaubagaimanapun, rawatan hababermangkin yang biasa digunakan adalah mahal disebabkan pengaplikasian mekanisme pemanasan lazim yang menggunakan tenaga elektrik yang tinggi. Kaedah alternatif pemanasan gelombang mikro adalah kos efektif, mudah dan berpotensi untuk proses skala besar.

Ketuhar gelombang mikro komersial yang diubah suai telah dibangunkan dan dicirikan untuk rawatan tar hababermangkin. Pada mulanya, penyingkiran tar dikaji dengan menggunakan sebatian model tar (toluena dan naftalena), diikuti oleh tar sebenar dari gas pengeluar yang diperolehi daripada pengelasan biojisim. Dua rawatan telah dijalankan: rawatan terma dan rawatan bermangkin. Spesies tar dan gas masing-masing dianalisa menggunakan Kromatografi Gas-Permeteran Spektrum Jisim (GC-MS) dan Kromatografi Gas-Terma Kekonduksian Pengesan (GC-TCD). Sementara itu, hampas/jelaga yang terendap pada permukaan pemangkin telah ditentukan menggunakan Penganalisis Permeteran Graviti Haba (TGA).

Keputusan eksperimen menunjukkan bahawa proses pemanasan terma di bawah penggunaan tenaga penyinaran gelombang mikro yang rendah adalah sesuai

untuk rawatan tar hababermangkin. Bagi model tar, kira-kira 91% daripada kedua-dua toluena dan naftalena masing-masing telah disingkirkan semasa rawatan terma pada suhu 1050°C dan 1200°C. Dalam rawatan pemangkin, kira-kira 76% toluena dan 67% naftalena masing-masing telah disingkirkan dengan dolomit pada suhu 850°C dan 900°C, manakala kira-kira 83% toluena dan 79% naftalena telah disingkirkan dengan menggunakan Y-zeolite pada suhu 700°C. Bagi tar sebenar, rawatan terma telah menjana nilai pemanasan tertinggi iaitu 5.76 MJ Nm⁻³ pada 1200°C, manakala penukaran tar dan partikel tertinggi masing-masing sebanyak 97% dan 98% dalam gas pengeluar diperolehi oleh dolomit pada 900°C. Secara umum, kadar tindakbalas penukaran tar khususnya rawatan terma di bawah penyinaran gelombang mikro adalah empat kali ganda secara purata lebih cepat berbanding dengan mekanisma pemanasan lazim manakala bagi rawatan bermangkin tidak ada perbezaan yang ketara daripada kadar tindakbalas.

TAR REMOVAL FROM PRODUCER GAS VIA THERMAL AND CATALYTIC MEANS IN A MICROWAVE REACTOR

ABSTRACT

Tar in biomass producer gas should be removed to avoid blocking of the pipe lines and to allow producer gas utilization in Internal Combustion (IC) engines and turbines for power generation. Among the available tar removal methods, thermal and catalytic (thermocatalytic) treatments of tar are more attractive with improvement of the producer gas energy content by converting tar into combustible gases. However, the commonly applied thermocatalytic treatments are costly by the use of conventional heating mechanism that consumes high electrical energy. The alternative method of microwave heating is cost effective, simple and potential for process scale up.

A modified commercial microwave oven was developed and characterized for thermocatalytic treatment of tar. Tar removal was conducted initially using tar model compounds (toluene and naphthalene) followed by real tar from producer gas derived from biomass gasification. Two treatments were conducted: thermal and catalytic treatments. Tar species and gases were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography-Thermal Conductivity Detector (GC-TCD), respectively. Whilst, coke/soot deposited on the catalysts was determined using Thermogravimetric Analyzer (TGA).

The experimental results showed that thermal heating process under low energy consumption of microwave irradiation is suitable for thermocatalytic treatment of tar. For tar model, about 91% of both toluene and naphthalene were removed during thermal treatment at temperatures of 1050°C and 1200°C,

respectively. In catalytic treatment, about 76% toluene and 67% naphthalene were removed using dolomite at temperatures of 850°C and 900°C respectively, whereas about 83% toluene and 79% naphthalene were removed using Y-zeolite at temperatures of 700°C. For real tar, thermal treatment generates the highest heating value of 5.76 MJ Nm⁻³ at 1200°C, whilst the highest tar and particle conversions of 97% and 98% respectively in the producer gas were provided by dolomite at 900°C. In general, for thermal treatment the reaction rate of tar conversion under microwave irradiation was four times faster on average than those of conventional heating mechanism whilst for catalytic treatment there was no significant difference of reaction rate.

CHAPTER 1 – INTRODUCTION

1.1 Research background

Fast depletion of the fossil-based energy reserves, increase in energy consumption and greater environmental awareness for global climate change due to CO₂ emissions have encouraged studies to look for greener sources of energy as alternatives to replace the fossil fuels. Therefore, research activities on renewable energy sources have become more and more important.

According to the Renewable Energy Policy Network for the 21st Century, renewable energy supplied approximately 19% of global final energy consumption by the end of 2011 as shown in Figure 1.1, an increase of about 12% from 2010 (REN21, 2013). Among all renewables, biomass is the most widely used energy source worldwide. However, almost half of renewable energy came from inefficient traditional biomass process for cooking and heating in developing countries.

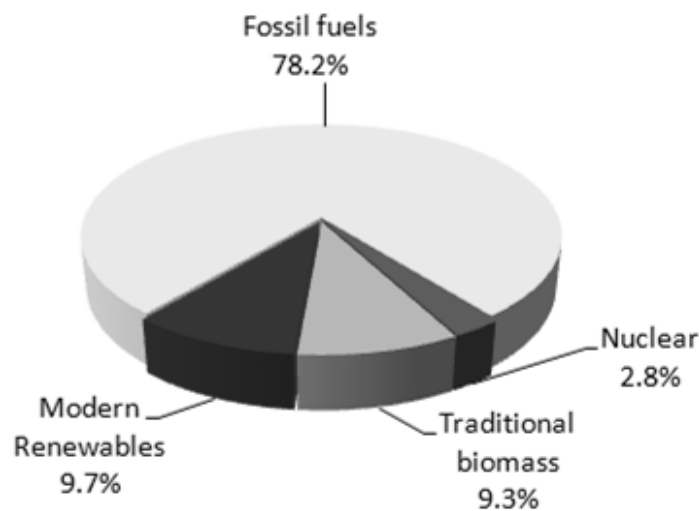


Figure 1.1: Estimated renewable energy share of global energy consumption in 2011 (REN21, 2013)

Thermo-chemical process is an efficient conversion of biomass into energy. One of the thermo-chemical processes is biomass gasification. In this process, biomass is converted into other forms of energy in the presence of an externally supplied gasifying agent such as steam, air or pure oxygen. It essentially occurs in three stages namely: drying where inherent moisture in the biomass fuel is removed, pyrolysis where volatile matters are released, and finally gasification where char and volatile matters are partially oxidized. The main product of biomass gasification is a combustible gas (producer gas), primarily composed of hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and water. Producer gas can be exploited in Internal Combustion (IC) engines and turbines for electricity generation (McKendry, 2002). It has potential for rural electrification projects particularly in third world countries where biomass supplies from agricultural industries are abundant and where electricity supply from the grid is not available (Lim and Alimuddin, 2008). For instance, an Integrated Biomass Gasification and Combined Cycle (IGCC) developed in Sweden has a Lower Heating Value (LHV) of about $5\text{-}6 \text{ MJ Nm}^{-3}$ and produces 6 MWe of electricity (4 MWe from the gas turbine and 2 MWe from the steam cycle) and 9 MW of heat using $18 \text{ MW}_{\text{th}}$ equivalents of wood residues (Overend, 2004).

However, gasification produces not only producer gas, char and ash but also byproducts such as NO_x , SO_2 , particulates and tar. Byproducts in general cause erosion and corrosion on metals. The types of byproducts contained in the producer gas and potential problems that can be generated are (Belgiorno et al., 2003): 1) particulates which cause erosion of metallic components and environmental pollution; 2) alkali metals such as sodium and potassium cause corrosion of metal at high temperature because of the stripping off of their protective oxide layer; 3) fuel-

bound nitrogen could potentially cause emission problems by forming NO_x during combustion; 4) sulfur and chlorine (especially from coal) can lead to harmful pollutants and acid corrosion of metals; and 5) tar which can cause metallic corrosion and clog filters and valves. Producer gas from biomass gasification although provides benefits as an alternative fuel has severe problems caused by the byproducts. The most undesirable byproduct is tar which is difficult to be removed.

1.2 Tar Content and Existing Tar Removal Method

Tar formation during pyrolysis of biomass as part of the biomass gasification process is unavoidable. Tar is formed due to the depolymerization of cellulose, hemicellulose and lignin. Besides the nature of biomass, tar formation is highly affected by the types of gasifier. Typically tar contents contained in producer gas produced from downdraft, fluidized bed and updraft gasifiers are about 1 g Nm^{-3} , 10 g Nm^{-3} and 100 g Nm^{-3} respectively (Milne et al., 1998). In general, all current gasifier systems exhibit raw producer gas qualities that need additional gas cleaning for subsequent end user applications. Literature survey shows that tar content tolerances of downstream applications are very strict where tar contents up to 100 mg Nm^{-3} and less than 5 mg Nm^{-3} are allowed for internal combustion (IC) engines and gas turbines, respectively.

The tar composition and properties associated with the component and condensation behavior of the tar are considered as the most importance factors rather than its quantity (Bergman et al., 2003). It is believed that, when the dew-point of tar vapor is reduced to levels below the lowest expected temperature, fouling problems associated with condensation can be solved. Hence, the selectivity performance of tar

treatment either removed or converted into other species is a key issue for a successful application of biomass producer gas.

Since three decades ago, various producer gas cleaning methods have been developed and reported in numerous literatures with the aim to produce high quality producer gas for end user applications. In general, these methods are classified into two categories, namely: 1) primary method that improves gasifier design to treat tar in-situ and 2) secondary method that consists of mechanical and thermocatalytic treatments (Devi et al., 2003). Secondary methods for producer gas cleaning are expensive.

Although primary methods may be substantially more ideal, they have not provided satisfactory solutions. Some of the primary methods can produce low tar emissions. For instance, the amount of tar produced during steam gasification in a Fast Internally Circulating Fluidized-bed Gasifier (FICFB) of about 1 g Nm^{-3} has been obtained (Hofbauer et al., 1997). However, the main drawbacks of primary methods are limit in feedstock flexibility and scale-up, the production of waste stream, a decrease in cold gas efficiency and complex gasifier construction (Bergman et al., 2003).

Two approaches usually used in secondary method are wet and dry gas treatments. Wet gas treatment includes wet electrostatic precipitator, wet scrubber and wet cyclone. It has been reported that a venturi scrubbing system has high tar removal performance where tar concentrations below $20\text{-}40 \text{ mg Nm}^{-3}$ can be achieved with following disadvantages (Han and Kim, 2008):

- 1) since the producer gas is at a high temperature, reducing the temperature during wet gas cleaning can decrease the net energy efficiency of the process,

- 2) as water is commonly used as a scrubbing medium, extensive treatment of the waste water is needed before discharge. This is a capital intensive process, and
- 3) if the producer gas is utilized for high temperature applications, there is a net loss of energy for cooling and heating the producer gas.

Dry gas treatment is either mechanical/physical, plasma, thermal or catalytic treatment. Mechanical/physical treatment includes cyclone, rotating particle separator and filter (bag, baffle, ceramic and fabric filters). Adsorption technique is also included in this method. Similar with wet gas treatment, dry gas mechanical/physical treatment also has some drawbacks such as high capital cost, tar deposited in filter which could not be easily cleaned and tar accumulation on the filter and adsorber surface which would lead to eventual plugging. Generally, filters are not suitable for tar removal although it have been demonstrated successfully in some cases (Han and Kim, 2008). The main use of these devices is to capture particles from the producer gas. Plasma treatments have been also employed in some cases, however, they have several drawbacks such as limited lifetime of the pulsed power devices, high costs and high energy demand of the overall process (Chang, 2003).

Among the possible tar removal methods, thermal and catalytic (thermocatalytic) treatment of tar is rather promising because of the complete destruction of the tar instead of creating a waste stream which is difficult to dispose. Tar content is mainly a function of temperature. It will decrease as temperature increases due to cracking and reforming reactions.

1.3 Thermocatalytic treatment

Tar as one of the undesirable byproducts produced during biomass gasification processes is a major problem that has not been completely solved yet. When the vapor pressure of the tar exceeds its saturation pressure, the tar vapor becomes saturated and leads to condensation that can block downstream pipelines and foul engines and turbines. Therefore, removal or conversion of tar as well as particulates from producer gas is indispensable for power generation. For this purpose, implementation of thermocatalytic treatment is more favorable due to converting tar into useful gases such as hydrogen, carbon monoxide or hydrocarbon gases which can improve the producer gas energy content.

Thermal treatments of tar have been performed at temperature higher than 1100°C (Jess, 1996b, Zhang et al., 2010) that provides high tar removal efficiency. Previous study showed that the temperature of 1200°C and residence time less than 10 s are needed to achieve high tar removal efficiency (Jess, 1996b). Certainly, the high reaction temperatures require high energy that affects the overall efficiency making it uneconomical for practical application.

In another approach, catalytic treatment processes have gained more attention. In particular, there have been ongoing efforts for developing more economical catalysts for tar conversion. For this reason, the utilization of natural catalysts such as dolomite and zeolite or their impregnation on metal catalysts would be a wise choice. Calcined dolomite is a very well-known catalyst for tar removal that is inexpensive and prevents agglomeration (Corella et al., 2004b). Calcined dolomite was found to have better tar conversion activity in biomass gasification (Delgado et al., 1996, Delgado et al., 1997). Its activity also depends on where the natural dolomite is obtained due to different their chemical composition (Gusta et al.,

2009, Orío et al., 1997, Yu et al., 2009b). It was found that Swedish dolomite with high calcium/magnesium ratio and iron content has better tar conversion efficiency compared to Chinese dolomites (Yu et al., 2009b). The use of zeolites for biomass tar conversion has also been reported but is still rare. Zeolite is a commercial Fluid Catalytic Cracking (FCC) catalyst proven as an active tar removal catalyst and improves gaseous quality with relatively low-price. In most of the published literatures biomass tar model compounds were used instead of real tar from producer gas such as benzene, naphthalene and 1-methylnaphthalene (Buchireddy et al., 2010, Dou et al., 2003, Radwan et al., 2000). Recently, the applications of natural calcined zeolite to remove the tar from biomass gasification have been observed. (Mun et al., 2013, Chiang et al., 2012, Chiang et al., 2013). However, the fine particle size of zeolites makes it unsuitable for high flow rate in-situ catalytic tar decomposition (Corella et al., 2004b).

1.4 Problem Statement

Although various efforts of producer gas cleaning methods have been performed and proven technically effective as described above but from an economic point of view, efficient removal of tar still remains the major technical obstacle to the success in commercialization of biomass gasification technologies on a large scale. In general, overall process of existing thermocatalytic treatments of tar is costly and high energy demand. This is because majority of thermocatalytic treatment of tar research is directed at conventional heating mechanism using an external high electrical source where heat transfer occurs from the surface to the core of the material. Moreover, tar conversion reaction can also be limited within a conventionally/electrically heated reactor due to the heat/mass transfer limitations as

the heat is supplied from the external wall in most of the conventional heating reactors (Bhattacharya et al., 2011). Other disadvantages are slow heating process, high heat losses and high heat transfer resistance that can damage the reactor walls due to continuous electrical heating (Salema and Ani, 2011). Accordingly, there is a need for a more economical method.

In order to support the development and operation of a commercial tar thermocatalytic treatment method, it is desirable to have a simple and rapid test technique that is economically feasible. For this reason, implementation of microwave energy for thermocatalytic treatment of tar would be a more realistic option as an alternative method to solve the limitations of conventional heating method. In this method, the transfer of energy into the material occurs instantaneously through molecular interaction with the electromagnetic field (Thostenson and Chou, 1999). The volumetric heating of materials using microwave can result in significant energy savings, reduce process time, increase process yield and environmental compatibility (Bykov et al., 2001, Jones et al., 2002). The additional advantages of microwave heating in the field of waste treatment including off gas treatment are: (1) rapid heating and high temperature capabilities, (2) selective heating, (4) enhanced chemical reactivity, (4) rapid and flexible process that can also be made remote, (5) ease of control, (6) process equipment availability, compactness, cost, maintainability, (7) portability of equipment and process, (8) cleaner energy source compared to some more conventional systems, and (9) overall cost effectiveness/savings (Wicks et al., 1998). A more comprehensive review on the unique characteristics of microwave heating and its application for biomass pyrolysis has been reported by Yin (Yin, 2012) and Motasemi and Ani (Motasemi and Ani, 2012). The literature showed that microwave can save up to 80% energy for heating

in thermo-chemical processes of biomass (Baysar et al., 1988, El harfi et al., 2000, Zhao et al., 2010, Budarin et al., 2010, Shuttleworth et al., 2013). Therefore, in the present research, a modified microwave system for thermocatalytic treatment of tarry materials is developed. This research has high prospect in providing basic knowledge into the fundamentals of tar thermocatalytic treatment via microwave irradiation that is cost effective, simplicity and potential for process scale up. In addition, it is expected that the high electromagnetic irradiation intensity not only provides rapid heating and high temperature but also increases radical reactions that are responsible for tar removal.

1.5 Objectives of the Thesis

This research work deals with tar conversion by means of thermocatalytic treatment under microwave irradiation. For this purpose, a proper design as well as construction of microwave system is needed to allow thermocatalytic treatment process at high temperatures. Therefore, the objectives of this study can be summarized as follows:

- 1) to develop and characterize a microwave tar treatment system for thermocatalytic treatment of tar process.
- 2) to investigate thermocatalytic treatment of tar model compounds and real tar from biomass producer gas under microwave irradiation.
- 3) to develop a mathematical reaction kinetic model of thermocatalytic treatment of tar model compounds and real tar from biomass producer gas.
- 4) to evaluate the performance of the microwave tar treatment system through mass and energy balance determinations and the potential for scaling up of the system.

1.6 Scope of the Thesis

The work presented here concerns the development and application of microwave energy as a new heating strategy in both thermal and catalytic treatment of tarry material. The microwave system contains silicon carbide (SiC) as absorber material within the reactor. Two natural, commercial and low-cost catalysts i.e. dolomite and Y-zeolite were also used to remove the tar effectively. With the aim to obtain optimal conditions and achievable technical performance for the new microwave tar thermocatalytic treatment process in term of temperature evolution within the reactor, various parameters including absorber material particle size, gas flow rate, bed height, and microwave power were tested.

In order to examine the capability of microwave thermocatalytic treatment reactor in removing tar, toluene and naphthalene as tar model compounds were used initially to simulate the real tar from producer gas. The evaporated toluene or naphthalene was then removed via thermal and catalytic treatment using dolomite and Y-zeolite at various temperatures and gas residence times. Stability test of the catalysts, however, was not addressed in this work. In thermocatalytic treatment of real tar, producer gas containing tar and particulates was continuously produced from gasification of rubber wood in a throatless suction downdraft gasifier. The yield of products particularly tar was presented in term of gravimetric yield.

The resulting data was used to develop the reaction kinetic model in both tar model compounds and real tar from producer gas studies. Finally, this study also evaluates mass and energy balances across the microwave reactor for thermocatalytic treatment of real tar from producer gas under investigated conditions. The potential for scaling up of the microwave system was also analyzed and evaluated.

1.7 Outline of the Thesis

The thesis is divided into five chapters which consist of introduction, literature review, methodology, results and discussion, and conclusions. Details of the thesis outline are described as follow:

Chapter 1: Introduction covers renewable energy share of global energy consumption and the potential utilization as well as several problems related with byproducts of producer gas from biomass gasification for power generation. Tar contents as a byproduct contained in producer gas produced from various gasifiers and overview of various tar removal methods are covered. The problem statement is included in this chapter for identification of the issues of the current study. The objectives of the present work are given as the solution of those issues. The scope of this work covers the research activities to reach these objectives.

Chapter 2: It provides literature review that covers biomass gasification processes in downdraft gasification, tar formation, definition and classification followed by literature review on tar removal methods especially thermal and catalytic treatment methods. Additionally, related theory about microwave energy is also presented. The chapter critically reviews recent studies.

Chapter 3: This chapter gives details about the experimental set-up for the investigation of the microwave thermocatalytic treatment of tar. The details of the materials used throughout of this study are described. The equipments for the sampling and analyses of products including tar, soot/particles and gases are presented and explained. Determination of coke deposited on catalysts is also given.

Chapter 4: Results and discussion are divided into six sections: (1) thermal heating characteristic of microwave reactor, (2) thermocatalytic treatment of tar model compounds, (3) reaction kinetic model of tar model compounds, (4) thermocatalytic

treatment of tar from producer gas, (5) global reaction kinetic model of tar from producer gas and (6) mass and energy balance closure across the microwave reactor in the case of thermocatalytic treatment of tar from producer gas. Scale up and assessment of energy production are also covered and discussed. In general, the obtained data is discussed and compared to other studies on thermocatalytic treatment of tar reported in the literatures.

Chapter 5: Summarizes the findings and gives the conclusions of the present study. Based on the present results, recommendations are also given for further research in this area.

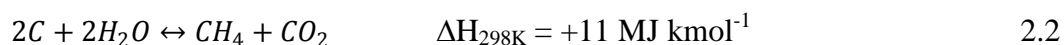
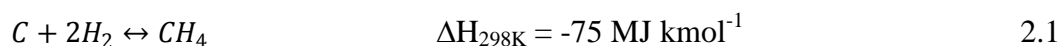
CHAPTER 2 – LITERATURE REVIEW

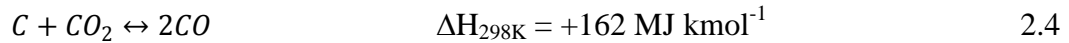
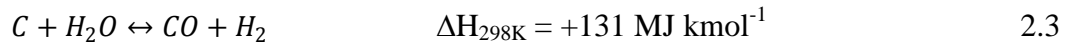
2.1 Biomass Gasification

Gasification is a proven technology for converting solid organic materials including coal and biomass into combustible gases (commonly known as producer gas). Investigation on gasification was first performed by Thomas Shirley in 1659 who conducted experiments with “carburetor hydrogen” (now called methane) and discovered gas from coal mine (Basu, 2010). During World War II biomass gasification was used for transportation, electricity and heat (Reed et al., 1988). Gasification takes place at high temperature in the presence of a gasifying agent such as air, oxygen, steam or a combination of them. Heat is supplied to the gasifier either directly using air or oxygen through exothermic reactions or indirectly from the outside of the reactor to raise the gasification temperature. During biomass gasification, typical processes include drying, pyrolysis, combustion and reduction or char gasification. Although these processes are frequently modeled in sequence, they often overlap as there is no sharp boundary between them and each can be assumed to occupy a separate zone (Rajvanshi, 1986, Basu, 2010).

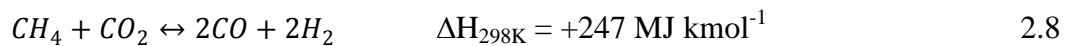
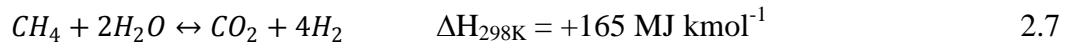
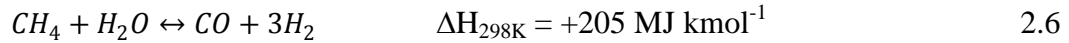
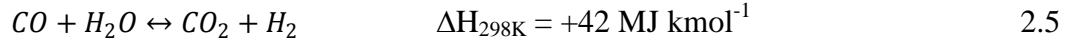
When gasification agents are introduced, oxidation reaction of biomass pyrolysis products proceed to provide the required heat for the whole gasification process as presented in the following reactions (Sutton et al., 2001b, Basu, 2010, Devi et al., 2003):

a. Carbon gasification:

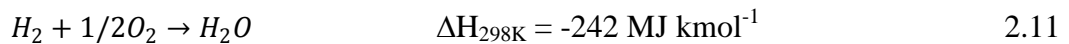
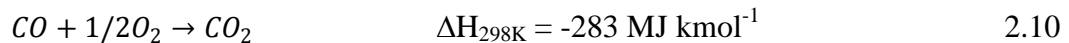
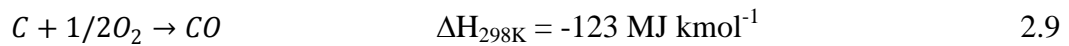




b. Gas reforming:



c. Partial oxidation:



There are two mainly categorized gasifiers for gasification of biomass according to the types of bed namely fixed bed and fluidized bed gasifiers (Warnecke, 2000). Fixed bed gasifier can be classified further as crossdraft, updraft and downdraft whereas fluidized bed gasifier can be either a bubbling fluidized bed or a circulating fluidized bed (Kumar et al., 2009). Table 2.1 compares the advantages and disadvantages of commonly found gasifiers in biomass gasification (Belgiorno et al., 2003, Basu, 2010, Warnecke, 2000). One of the key information given in the table is downdraft and crossdraft fixed bed gasifiers have relatively lower production of tar compared to other gasifiers. This feature makes the producer gas generated to be the most appropriate to use in internal combustion engines and turbines for power generation. Special highlights of downdraft fixed bed gasifier used in this work are discussed in the following section.

Table 2.1. Comparison of various gasifiers (Belgiorno et al., 2003, Basu, 2010, Warnecke, 2000)

Reactor	Type	Advantages/Disadvantages	Power production
Fixed bed	Updraft	Higher heating value, moderate dust content, high tar content	Small to medium scale
	Downdraft	Low tar content, moderate dust content, low heating value	
	Crossdraft	Low tar content, moderate dust content, low heating value, high pressure drop	
Fluidized bed	Bubbling	Improved mass and heat transfer from fuel, higher heating value, higher efficiency, moderate tar content, low carbon conversion	Medium to high scale
	Circulating	Higher mass and heat transfer from fuel, higher heating value, higher efficiency, higher carbon conversion, moderate tar content, moderate dust content	

2.1.1 Downdraft Gasifier

Reaction zones in a downdraft gasifier are somewhat different from those in the updraft gasifier where the locations of the combustion and gasification zones are interchangeable. In downdraft gasifiers, biomass is fed from the top and the gasifying agent is introduced above the gasification zone from the sides of the reactor. The pyrolysis products flow downward to the high temperature combustion zone and react with the gasifying agent as well as the moisture vaporized from the biomass for further decomposition. The hot producer gas exits at the bottom of the gasifier at moderate temperature of around 700°C and leaves the gasifier at a temperature between 200°C-350°C (Jain and Goss, 2000, Dogru et al., 2002).

Downdraft gasifiers are basically categorized into two types: throated and throatless gasifiers as visualized in Figure 2.1. Throated gasifiers have the

advantages of reducing the tar content and thus improving producer gas quality since the high temperature of this narrow zone provides a uniform temperature distribution over the cross-section and allows most of the tar contained in the pyrolysis products to crack (Reed and Das, 1988, Basu, 2010). Temperature at the combustion zone is around 900°C to 1200°C that is enough to generate producer gas with tar content of typically less than 0.1% by weight or 0.5 gNm⁻³ (Reed and Das, 1988).

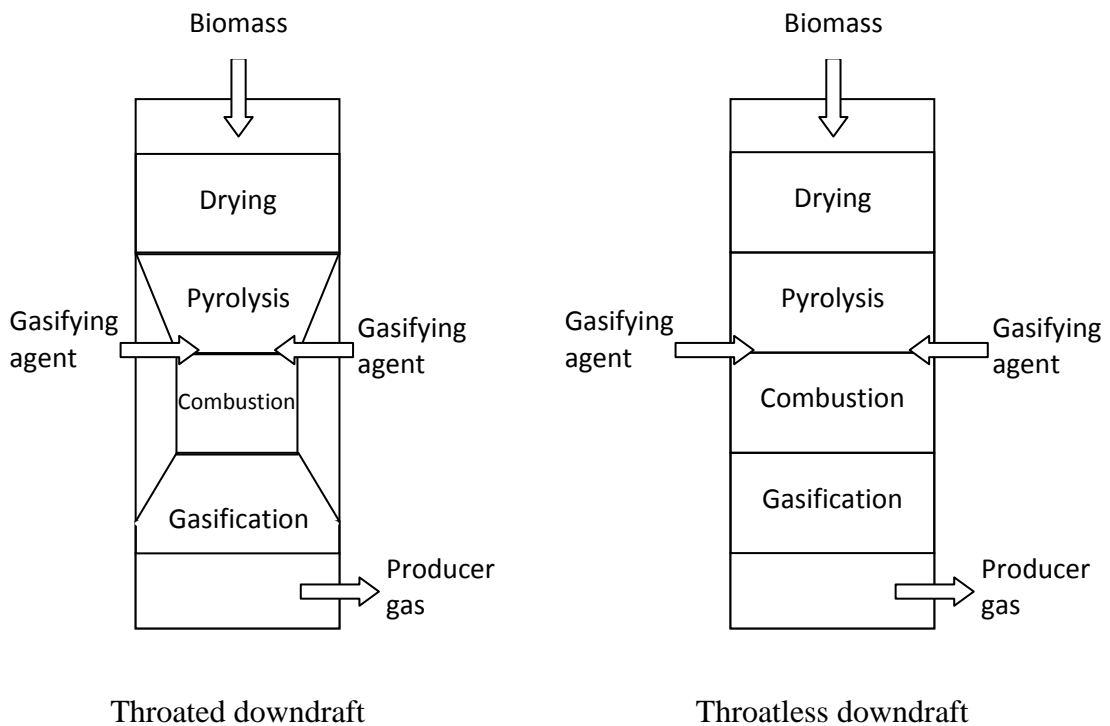


Figure 2.1: Throated and throatless fixed bed downdraft gasifier along with gas/biomass flow directions and reaction zones. Adapted from Basu (2010)

Stratified or suction gasifier is one of the throatless gasifier designs where the top is exposed to the atmosphere. The open top ensures uniform access of gasifying agent (air or oxygen) to the pyrolysis zone by the suction created downstream of the gasifier. The uniform passage of air and biomass down the gasifier keeps high local temperatures to be constant. A throatless design allows unrestricted movement of the

biomass down the gasifier that avoids bridging or channeling, which might occur in the throated type (Reed and Das, 1988, Basu, 2010).

2.1.2 Gasifier Performance

During biomass gasification, various parameters such as properties of the biomass fuel, particle size, gasifying agent, temperature, pressure, equivalence ratio, bed additive and type of the gasifier affect the performance of biomass gasifier. It is usually represented by the quantity and quality of the producer gas generated. In general, cold gas efficiency and heating value are the important parameters in determining the amount of biomass converted into gas and the quality of the producer gas, respectively (Jain and Goss, 2000, Reed and Das, 1988, Basu, 2010). Cold gas efficiency (η_{cg}) can then be defined as the energy content of the producer gas in comparison to that of biomass fuel as expressed below (Jain and Goss, 2000).

$$\eta_{cg} = \frac{LHV_{PG} Q_{PG}}{LHV_b \dot{m}_b} \times 100 \quad 2.12$$

where:

LHV_{PG} = lower heating value of the producer gas (MJ Nm^{-3})

Q_{PG} = volumetric flow rate of the producer gas ($\text{Nm}^3 \text{h}^{-1}$)

LHV_b = lower heating value of the biomass fuel (MJ kg^{-1})

\dot{m}_b = mass flow rate of the biomass fuel (kg h^{-1})

Based on the producer gas composition, LHV_{PG} can be calculated and is dependent on the percentage volume fraction of H_2 , CO and CH_4 as follow:

$$LHV_{PG} = x_{\text{H}_2} LHV_{\text{H}_2} + x_{\text{CO}} LHV_{\text{CO}} + x_{\text{CH}_4} LHV_{\text{CH}_4} \quad 2.13$$

where x is the volume fraction of each gas and the LHV of each gas is 10.757, 12.641 and 35.787 MJ Nm^{-3} for H_2 , CO and CH_4 , respectively (Waldheim and Nilsson, 2001).

Table 2.2 shows the comparison of several parameters from different gasifiers. As can be seen from the table that apart from the gasifier types and typical heat output, the different gas compositions depend on the fuel moisture whilst the LHV of producer gas for all gasifier given in the table is relatively similar (Bridgwater, 2003, Morf, 2001, Paasen et al., 2002).

Table 2.2. Comparison of several parameters from various gasifiers (Bridgwater, 2003, Morf, 2001, Paasen et al., 2002)

Parameter	Unit	Fixed bed		Fluidized bed	
		Updraft	Downdraft	Bubbling	Circulating
Typical heat output	kW _{th}	1.000-10.000	100-1.000	<25.000	<100.000
Fuel moisture	wt.% (daf)	52	6	14	15
CO ₂	vol.%	10.0	11.5	16.7	15.0
CO	vol.%	20.0	22.5	15.8	15.4
H ₂	vol.%	14.0	21	9.3	14.8
CH ₄	vol.%	2.5	1.5	3.8	4.2
LHV	MJ Nm ⁻³	4.9	5.6	4.4	5.0
Particles	g Nm ⁻³	0.1 – 0.5	0.1 – 1	1-10	20 - 60
Tar	g Nm ⁻³	50 – 150	0.5 – 2	1-23	7 – 10

daf : dry and ash-free basis

The table above also shows ranges of particle and tar contents in the producer gas. Particle contents contained in the producer gas from fluidized bed gasifiers are significantly higher than from fixed bed gasifiers due to the small fuel particles required and the high operating gas velocities. In the case of tar, the highest tar contents contained in the producer gas are found from updraft gasifiers due to the pyrolysis gas is swept to the gasifier outlet without passing a hot char zone where secondary tar reactions could occur. The tar content of producer gas from fluidized beds mainly depends on the temperatures and the gas residence times in the reactor (Morf, 2001).

2.1.3 Tar Formation, Definition and Classification

2.1.3(a) Tar Formation

As elucidated earlier, biomass gasification is a complex process that generally occurs in the sequence of stages of drying, pyrolysis, oxidation and reduction. A schematic of the process as well as products generated is presented in Figure 2.2 (Basu, 2010).

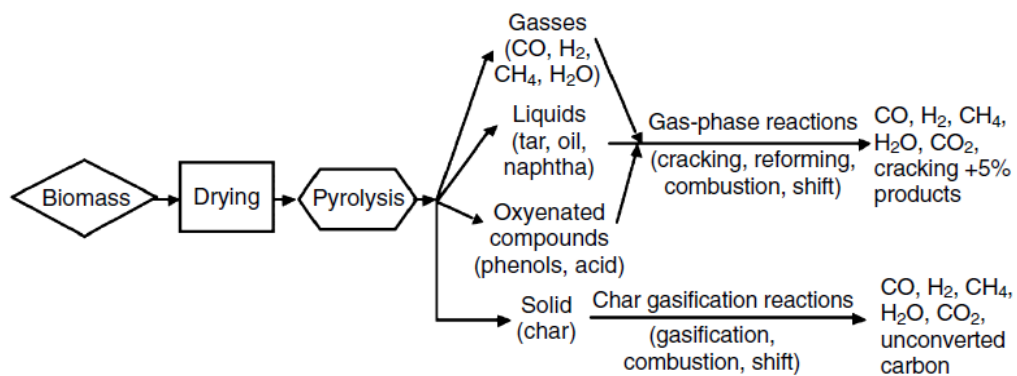


Figure 2.2: Gasification pathways (Basu, 2010)

During biomass gasification, tar is formed primarily as a product through depolymerization from the pyrolysis stage at a relatively low temperature of 200°C to 500°C. In this condition the cellulose, hemicellulose and lignin components of biomass break down into primary tar that contains oxygenates and primary organic condensable molecules (Milne et al., 1998). As the temperature increases above 500°C, the primary tar compounds undergo decomposition into smaller molecules, gases and heavier molecules called secondary tar. Further increase of temperature, primary tar products is destroyed and tertiary products are formed as given in Figure 2.3.

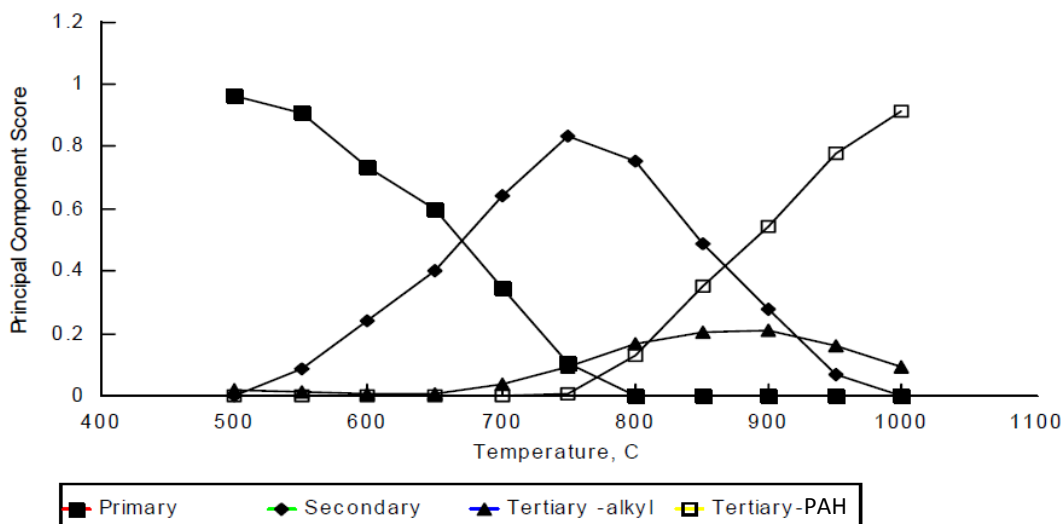


Figure 2.3: Tar formation as a function of temperature (Milne et al., 1998)

2.1.3(b) Tar Definition and Classification

Several definitions of tar have been reported in the literatures. It is basically affected by the quality of producer gas required for a particular end user application and the method of tar sampling and analysis. One of the definitions as follows: tar is the organics (generally assumed to be largely aromatic) produced under thermal or gasification of any organic material (Milne et al., 1998). However, the non-condensable products such as benzene, ethylene and cyclopentadiene are also termed as tar when the producer gas is used for several types of fuel cell applications. Tar is also defined as a complex mixture of condensable hydrocarbons, comprise of single to multiple ring aromatic compounds along with other oxygen containing hydrocarbons and complex Poly-cyclic Aromatic Hydrocarbons (PAH) (Devi et al., 2005c) or hydrocarbons with molecular weight higher than benzene (Maniatis and Beenackers, 2000).

On the one side, tar compounds are classified into four classes based on the reactivity of tar compounds, namely: primary products (cellulose-derived,

hemicellulose-derived and lignin-derived), secondary products (phenolics and olefins), alkyl tertiary products (mainly methyl derivatives of aromatic compounds) and condensed tertiary products (PAH series without substituent) (Milne et al., 1998). On the other side, tar compounds can also be classified into five classes based on chemical, solubility and condensability of tar components as shown in Table 2.3 (Devi et al., 2005c, Li and Suzuki, 2009, Abu El-Rub, 2008).

Table 2.3. List of tar compounds that are considered for different tar classes (Devi et al., 2005c, Li and Suzuki, 2009, Abu El-Rub, 2008)

Tar class	Class name	Property	Representative compounds
1	GC-undetectable	Very heavy tar, cannot be detected by GC	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar
2	Heterocyclic	Tar containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, Dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2–3 rings)	2 and 3 rings compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4–7 rings)	Larger than 3-ring, these components condense at high-temperatures at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

The available list of tar components that may be found in the producer gas tar samples produced from biomass gasification in various gasifiers are tabulated in Table 2.4 (Paasen et al., 2002). Tar compounds that are analyzed less frequently or occur in lower concentrations are typed in *italics* in the table.

Table 2.4. The available list of tar compounds from various gasifier (Paasen et al., 2002)

Downdraft/Fluidized bed gasification	Pyrolysis and Updraft gasification
<p>Phenols Phenol <i>Cresols (o, m or p)</i> <i>Xylenols</i> <i>(Methyl)Naphthols</i></p> <p>Furans <i>Benzofuran</i> <i>Methylbenzofurans</i> <i>Dimethylbenzofurans</i> <i>Dibenzofuran</i></p> <p>Aromatic compounds Benzene Toluene Xylenes (o, m and p) <i>Ethynylbenzene</i> <i>Styrene</i> Indene (1H-Indene) Methylindene</p> <p>PAHs Naphthalene* (1- or 2-) Methylnaphthalene Diphenyl Acenaphthylene* Acenaphthene* Fluorene* (9H-Fluorene) Phenanthrene* Anthracene* Fluoranthene* Pyrene* Benzo(a,b,c) fluorene <i>Benzo(a)anthracene*</i> Chrysene* <i>Benzo(b*, j or k*)fluoranthene</i> <i>Benzo(a* or e)pyrene</i> <i>Dibenzo(a,h)anthracene*</i> <i>Perylene</i> <i>Indeno(1,2,3-cd)pyrene*</i> <i>Benzo(g,h,i)perylene*</i> <i>Dibenzopyrenes</i> <i>Anthanthrene</i> <i>Coronene</i></p>	<p>Acids Formic acid Propionic acid Butyric acid Acetic acid</p> <p>Sugars Levoglucosan <i>Alpha-D-Glucose</i> <i>Beta-D-Fructose</i> <i>Cellobiosan</i></p> <p>Alcohols and phenols <i>Methanol</i> <i>Ethanol</i> Phenols Cresols (o, m or p) Xylenols</p> <p>Aldehydes and ketones <i>Formaldehyde</i> <i>Acetaldehyde</i> <i>Acetone</i> <i>2-Cyclopenten-1-one</i> <i>(Methyl)- 2-Cyclopenten-1-one</i></p> <p>Guaiacols Guaiacol Creosol (= 4-methyl-guaiacol) Ethylguaiacol Eugenol Isoeugenol</p> <p>Furans Dimethylfuran Furfural (2-furaldehyde) Methyl Furfural Furfuryl alcohol <i>(Methyl- or dimethyl-) benzofurans</i> <i>Dibenzofurans</i></p> <p>Mixed oxygenates Hydroxyacetaldehyde Acetol Vanillin</p>

Downdraft/Fluidized bed gasification	Pyrolysis and Updraft gasification
Nitrogen containing aromatics	Propanal-2-one
Pyridine	Glyoxal
Methylpyridines	<i>2-hydroxy-3-methyl-2-cyclopentene-1-one</i>
Picolines	<i>(di-, tri-)Methoxybenzenes</i>
(Iso)Quinoline	<i>Trimethoxyphenols</i>
	Aromatic compounds
	Benzene
	Toluene
	Xylenes (o, m and p)
	Ethynylbenzene
	Styrene
	Indene (1H-Indene)
	Methylindene
	PAHs
	Naphthalene*
	(1- or 2-) Methylnaphthalene
	<i>Diphenyl</i>
	Acenaphthylene*
	<i>Acenaphtene*</i>
	Fluorene* (9H-Fluorene)
	<i>Phenanthrene*</i>
	<i>Anthracene*</i>
	<i>Fluoranthene*</i>
	<i>Pyrene*</i>
	Nitrogen containing aromatics
	(Methyl)pyridines
	Picolines
	<i>(Iso)Quinoline</i>

* : indicate EPA list of 16 PAHs

From the table above, it can be concluded that tar compounds produced from downdraft gasifiers are mainly composed of light aromatic and light poly-aromatic hydrocarbons that are classified into classes 3 and 4 tar, respectively. On the other hand, updraft gasifiers mainly produced heavy oxygenated-based tar compounds and heterocyclic compounds that are classes 1 and 2 tar, respectively.

Tar presents as the main obstacle in biomass gasification for not only causing serious operational problems in downstream pipeline and end user application but

also influence the energy efficiency of the overall process. Typical values of producer gas quality requirement for IC engines and gas turbines as power generators are tabulated in Table 2.5. As shown, IC engines are more tolerant of contaminants particularly tar than turbines due to the relatively high combustion temperature in the combustion chamber (cylinder).

Table 2.5. Producer gas quality requirement for power generator (Milne et al., 1998)

Power generators	Particles (mg Nm ⁻³)	Particle size (μm)	Tar (mg Nm ⁻³)	Alkali metals (mg Nm ⁻³)
IC engine	< 50	< 10	< 100	-
Gas turbine	< 30	< 5	< 5	0.24

In the case of tar, this problem is fundamentally not only concerned with the quantity, but also the composition and properties of the tar that are associated with the component and condensation behavior of tar, respectively. Figure 2.4 shows the relation between the dew-point and concentration of tar (Bergman et al., 2003). It can be seen that only classes 2 and 4 tar play important role in this matter, dependent on the concentration in the producer gas.

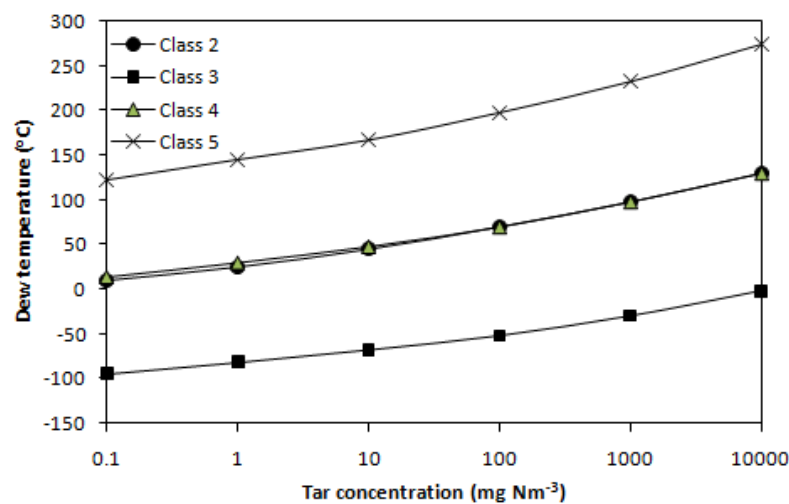


Figure 2.4: Relation between tar dew-point and concentration (Bergman et al., 2003)