



UNIVERSITI PUTRA MALAYSIA

**MATHEMATICAL MODELS FOR TAR CRACKING AND CHAR
REACTIONS IN A BUBBLING FLUIDISED BED REACTOR**

AHMED ABDULMAJEED MOHAMMED AL-OGAIDI

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By

AHMED ABDULMAJEED MOHAMMED AL-OGAIDI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

January 2019

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DEDICATION

Thanks to ALLAH the most merciful
To my beloved father and mother, I appreciate your sacrifice, care, and support to
achieve my dreams

To my beloved wife and children (Farah and Adham), I am grateful for your support
To my beloved uncles and my brother, thank you for the support



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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January 2019

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Tar is a contaminant product produced from the devolatilisation of the biomass in the gasification process which consists of a collection of organic compounds. The formation of tar depends on the gasifier setup and operating conditions, and can cause blockage in downstream equipment and facilities. Therefore, it is essential to reduce its levels through examining the effects of the parameters on its formation. In this research, two separate models were built to represent devolatilisation stage in the upper part and fluidized-bed stage in the down part of a lab-scale fluidized-bed gasifier of top feeding configuration.

The upper part of the reactor was modelled using a pseudo-equilibrium model (PEM) which employed yield correlations for tar, bio-oil, char, gas composition, and CH_4 obtained from experimental work at temperature range of 650 – 850°C. Two parameters were investigated: temperature (650 – 850°C) and carrier gas flow rate (10 – 30 L/min). The results showed a good prediction for tar yield with low root mean square (RMS = 0.003) compared to experiments, and conversion (59.7%) compared to experiments (51.5%) at 850 °C. The change of flow rate showed slightly increase of tar yield. Fair predictions obtained for other products.

The down part of the reactor was modelled for the gasification reactions of char using two-phase model. The char diffusion equation was imposed in the model to estimate the carbon conversion and oxygen consumption. Moreover, the effects of two parameters on char reactions were investigated: temperature (650 – 850°C) and equivalence ratio (ER) (0.2 – 0.4). The results showed that carbon conversion, oxygen consumption and final tar yield were 33 wt%, 66 vol.%, and 5 g/Nm³, respectively. Meanwhile, the yield of CO increased progressively while CO_2 increased considerably when temperature increased. The change of ER (0.2 – 0.4) decreased the yield of CO and CO_2 .

The temperature has a major effect on the tar yield and conversion in the upper part of the reactor. Meanwhile, the implication of a correction factor for steam reforming reaction (SRMR) in the PEM is important for better predictions of the yield of CO and CH₄ produced from the devolatilisation. On the other hand, the high location of the feeding point reduces the carbon conversion and oxygen consumption, and decouples the reactions of tar with O₂ and CO₂ which consequently reduce the yield of H₂ and CO.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMODELAN PENGGASAN TANAN BUAH KOSONG DALAM REAKTOR LAPISAN TERBENDALIR GELEMBUNG

Oleh

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Tar adalah produk pencemar yang dihasilkan daripada penyahmeruapan biomas dalam proses pengelasan yang terdiri daripada pengumpulan sebatian organik. Pembentukan tar bergantung kepada penyediaan pengelas dan keadaan kendalian, dan boleh menyebabkan halangan pada peralatan dan kemudahan hilir. Oleh itu, adalah penting untuk mengurangkan tahapnya dengan mengkaji kesan parameter terhadap pembentukan tar. Dalam kajian ini, dua model berasingan telah dibina untuk mewakili peringkat penyahmeruapan di bahagian atas dan lapisan terbendalir di bahagian bawah pengelasan lapisan terbendalir tatarajah suapan atas.

Bahagian atas reaktor dimodelkan dengan menggunakan model pseudo-keseimbangan (PEM) yang menggunakan korelasi hasil untuk tar, bio-minyak, arang, kandungan gas, dan CH_4 yang diperolehi daripada kerja uji kaji pada julat suhu $650 - 850^\circ\text{C}$. Dua parameter telah disiasat: suhu ($650 - 850^\circ\text{C}$) dan kadar aliran gas pembawa ($10 - 30 \text{ L/min}$). Keputusan menunjukkan ramalan yang baik untuk hasil tar dengan punca min kuasa dua yang rendah ($\text{RMS} = 0.003$) berbanding dengan uji kaji, dan penukaran (59.7%) berbanding dengan uji kaji (51.5%) pada 850°C . Perubahan kadar aliran menunjukkan sedikit peningkatan hasil tar. Ramalan yang sederhana diperolehi untuk produk lain.

Bahagian bawah reaktor dimodelkan untuk tindakbalas pengelasan arang menggunakan model dua fasa. Persamaan peresapan arang telah dikenakan dalam model untuk menganggarkan penukaran karbon dan penggunaan oksigen. Tambahan lagi, kesan dua parameter terhadap tindakbalas arang telah disiasat: suhu ($650 - 850^\circ\text{C}$) dan nisbah kesetaraan (ER) ($0.2 - 0.4$). Keputusan menunjukkan penukaran karbon, penggunaan oksigen dan hasil tar akhir adalah 33% berat, 66% isipadu, and 5 g/Nm^3 , masing-masing.

Sementara itu, hasil CO meningkat secara progresif manakala CO₂ meningkat dengan ketara apabila suhu meningkat. Perubahan ER (0.2 – 0.4) menurunkan hasil CO dan CO₂.

Suhu mempunyai kesan utama pada hasil tar dan penukaran di bahagian atas reaktor. Sementara itu, implikasi faktor pembetulan untuk tindakbalas pembentukan semula stim (SRMR) dalam PEM penting untuk ramalan yang lebih baik hasil CO dan CH₄ yang terhasil daripada penyahmeruapan. Sebaliknya, lokasi yang tinggi titik penyuaapan mengurangkan penukaran karbon dan penggunaan oksigen, dan menyahgandingkan tindakbalas tar dengan O₂ dan CO₂ di mana akibatnya menurunkan hasil H₂ dan CO.



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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS AND ACRONYMS

ASHSEP	Ash separator
BBM	Black-box model
BEM	Bubble assemblage model
BIGCC	Biomass Integrated Gasification Combined Cycle
BOD	Biochemical oxygen demand
CARBONSE	Carbon separator
CCBMM	Counter-current backmixing model
CFDM	Computational fluid-dynamics model
CHP	Combined heat and power
COD	Chemical oxygen demand
CPO	Crude palm oil
CRS	Chemical reaction stoichiometry
DCM	Dichloromethane
DECOMP	Decomposition
DHM	Davidson-Harrison model
DNS	Direct numerical simulation
DPM	Discrete particle model
EEM	Eulerian-Eulerian model
EFB	Empty fruit bunch
ELM	Eulerian-Lagrangian model
EM	Equilibrium model
EQUILI	Equilibrium
ER	Equivalence ratio

EU	European Union
FB	Freeboard
FBG	Fluidised-bed gasifier
FC	Fixed carbon
FFB	Fresh fruit bunch
FM	Fluidization model
GC	Gas chromatography
GHG	Greenhouse gases
HHV	High heating value
HMBM	Heat and mass balance model
ICE	Internal combustion engine
ID	Inside diameter
IEA	International Energy Agency
IGCC	Integrated gasification combined cycle
KLM	Kunii-Levenspiel model
LES	Large eddy simulation
LHV	Low heating value
LLM	Lagrangian -Lagrangian model
MF	Mesocarp fibre
MPOB	Malaysian Palm Oil Board
MS	Mass spectrometry
MZM	Multi-zone model
NSEP	Nitrogen separator
OPT	Oil palm trunk

OXNITSEP	Oxygen nitrogen separator
PAH	Polyaromatic hydrocarbon
PEM	Pseudo- equilibrium model
PFR	Plug-flow reactor
PKO	Palm kernel oil
PKS	Palm kernel shell
POME	Palm oil mill effluent
RMS	Root mean square
RMSE	Root mean squared error
SB	Sugarcane bagasse
SEM	Scanning electron microscope
TCD	Thermal conductive detector
TFM	Two fluid model
TG	Thermogravimetric
TM	Thermodynamic model
TPES	Total primary energy supply
VBA	Visual Basic for Applications
WATERSEP	Water separator
WGSR	Water-gas shift reaction
XRF	X-ray Fluorescence

LIST OF NOTATIONS

g	Gravity acceleration (9.8 m/s ²)
(conv) _i	Conversion of methane, bio-oil, and tar
ΔG	Gibbs free energy (kJ/mol)
(N ₂) _{required}	Total volume of nitrogen required to sweep gases (m ³)
(val) _n	Old predicted value
(val) _{n+1}	New predicted value
ρ_f	Density of fluid
C _a H _b O _d	Chemical formula of bio-oil
c _{g,i,b}	Gas species i concentration in bubble (mol/m ³)
c _{g,i,e}	Gas species i concentration in emulsion (mol/m ³)
C _m ^o H _y ^o	Hydrocarbon with lower molecular weight than tar
C _n H _m O _p	Chemical formula of biomass
C _n ^o H _x ^o	Tar
H _{C_aH_bO_d}	Low heating value of bio-oil (kJ/kg)
h _{C_aH_bO_d} ^o	Specific enthalpy of bio-oil (kJ/kg)
h _{H₂O} ^o	Specific enthalpy of water (kJ/kg)
h _{f,EFB} ^o	Enthalpy of formation of EFB (kJ/kg EFB)
h _{f,k} ^o	Enthalpy of formation of product (k) (kJ/mol)
h _C ^o	Specific enthalpy of carbon (kJ/kg)
h _{CO₂} ^o	Specific enthalpy of carbon dioxide (kJ/kg)
h _{O₂} ^o	Specific enthalpy of oxygen (kJ/kg)

$P_{i,\text{mod}}$	Predicted values
$P_{i,\text{exp}}$	Measured values
ρ_{EFB}	True density of EFB (kg/m^3)
ρ_{g}	Gas density (kg/m^3)
ρ_{p}	Density of particle
ρ_{s}	Solid density (kg/m^3)
$J_F^{-1}(x_n)$	Inverse of Jacobian matrix
$\ e\ $	Norm of residuals
ΔH_{298}°	Standard enthalpy of reaction
A	Cross section area of the bed (m^2)
a	Number of carbon atoms in bio-oil chemical formula
A^*	Form of unit matrix
A''	Mass percentage of ash (dry basis EFB)
a_1	Slope
A_e	Matrix of elements subscripts in their molecular form
A_f	Formula matrix
A_i	Peak area from GC analysis
Ar	Archimedes number
b	Number of hydrogen atoms in bio-oil chemical formula
b_1	Linear regression constant
b_e	Element-abundance vector
C	Mass percentage of carbon (dry basis EFB)
C'	Number of components in CRS calculations

C_d	Reactant species molar concentration into the dense phase
$c_{O_2,i,b}$	Concentration of oxygen in bubble at inlet (mol/m^3)
$c_{O_2,i,e}$	Concentration of oxygen in emulsion at inlet (mol/m^3)
c_{out}	Outlet concentration of CO and CO_2 (mol/m^3)
$C_p H_x O_h$	Chemical formula of EFB
C_p°	Heat capacity ($\text{J/K} \cdot \text{mol}$)
c_q	Concentration of CO and CO_2 at element q
d	Number of oxygen atoms in bio-oil chemical formula
Da	Damköhler number
daf	Dry ash free
d_{avg}	Particle average diameter (mm)
D_b	Mass diffusion coefficient in bubble phase (m^2/s)
db	Dry basis
d_{b0}	Initial bubble diameter (cm)
d_{b1}	Bubble diameter (cm)
d_{bm}	Maximum bubble diameter (cm)
DCOALIGT	Biomass density model in Aspen Plus
D_e	Mass diffusion coefficient in emulsion phase (m^2/s)
d_{eff}	Correspondent diameter of sphere particle (mm)
df	Degree of freedom
d_l	Lower limit of particle diameter in the range
d_p	Particle diameter (mm)
\bar{d}_p	Average particle size (mm)
d_{p1}	Biomass particle diameter (mm)

d_{pe}	Effective diameter (mm)
d_{psand}	Sand particle diameter (mm)
D_s	Dispersion coefficient for solid in axial direction (m^2/s)
D_t	Internal diameter of reactor (cm)
d_u	Upper limit of particle diameter in the range
dz	Infinitesimal element of bed height
E	Activation energy (kJ/mol)
e	Allowable error
E'	Number of elements incorporated in the system
E_{EFB}	Energy generation potential for EFB (PJ)
E_F	Energy generation potential for fibre (PJ)
E_S	Energy generation potential for shell (PJ)
E_T	Total energy (PJ)
E_{tol}	Tolerance
$F(x_n)$	Vector of initial values
F_{daf}	Amount of feed (g)
F_{gp}	Number of moles of produced gases per kilogram of EFB (mol gases produced/kg EFB)
\dot{F}_{gp}	Molar flow of gases (mol gp/s)
F_{N_2}	Flow rate of the nitrogen (L/min)
f_{WGSR}	Equilibrium Correction factor of water-gas shift reaction
H	Mass percentage of hydrogen (dry basis EFB)
h	Number of oxygen atoms in EFB chemical formula
H'	Percentage of hydrogen (as-received basis)

H_C	Low heating value of carbon (kJ/kg)
HCOALGEN	Biomass enthalpy model in Aspen Plus
H_f	Enthalpy of formation (kJ/mol)
h_g	Latent heat of steam
HHV_{EFB}	High heating value of EFB (kJ/kg EFB)
h°_C	Specific enthalpy of carbon (kJ/kg)
H_{oil}	Mass fraction of hydrogen in bio-oil
HS	High density- small particles
j	Number of hydrogen atoms in EFB chemical formula
k	Rate constant (s^{-1})
k_0	Pre-exponential factor (s^{-1})
K_1 and K_2	Constants
K_{be}	Mass exchange between bubble and emulsion (s^{-1})
K_{exp}	Experimental equilibrium constant of water-gas shift reaction
K_i	Response factor from GC analysis
K_{SRMR}	Equilibrium constant of methane steam reforming reaction
K_{WGSR}	Theoretical equilibrium constant of water-gas shift reaction
l and u	Indices of discretization in horizontal and vertical directions
LB	Lower density-big particles
LHV_{EFB}	Low heating value of EFB (kJ/ kg EFB)
M	Percentage of moisture (as-received basis)
m_1	Moles of carbon (wet basis)
m_2	Moles of hydrogen (wet basis)
m_3	Moles of nitrogen (wet basis)

m_4	Moles of sulfur (wet basis)
m_5	Moles of oxygen (wet basis)
M_{air}	Molecular weight of air (kg/kgmol)
M_C	Molar mass of carbon (g/gmol)
M_{Ch}	Molecular weight of char
M_{CO_2}	Molecular weight of carbon dioxide (g/gmol)
m_e	Vector of species moles
M_H	Molar mass of hydrogen (g/gmol)
$M_{\text{H}_2\text{O}}$	Molecular weight of water (g/gmol)
M_i	Individual gas species molecular weight (g/gmol)
$m_{i\%}$	Individual gas species mole percentage
m_{ij}	Number of moles of gas species at each sampling time
m_{iT}	Total number of moles of gas species in each run
MJ	Megajoule
M_N	Molar mass of nitrogen (g/gmol)
M_{N_2}	Molecular weight of N_2 (kg/kgmol)
m_{N_2}	Number of moles of nitrogen per kilogram of EFB
M_O	Molar mass of oxygen (g/gmol)
M_{O_2}	Molecular weight of oxygen (g/gmol)
$m_{p,i}$	Species i generated during unit time through pyrolysis in the bed (kmole/s)
MPa	Megapascal
M_S	Molar mass of sulfur (g/gmol)
Mt	Million tonnes

MW	Megawatt
MWhr	Megawatt-hour
m_x	Molar composition of known calibration gas mixture
N	Number of gas species
n^*	Reaction order
N^*	Mass percentage of nitrogen (dry basis EFB)
N'	Total sampling time (s)
N_c	Number of species in the system
n_d	Number of holes in the perforated plate
n°	Number of carbon atoms in tar chemical formula
N_s	Sample size
O	Mass percentage of oxygen (dry basis EFB)
P	Total pressure (atm)
p	Number of carbon atoms in EFB chemical formula
p_1, q_1, r_1	Stoichiometric coefficients in tar cracking chemical equation
PH	Acidity scale
p_i	Partial pressure
PJ	Petajoules
P°	Reference pressure (atm)
q	Number of elements
Q_0	Volumetric flowrate (m^3/h)
$Q_{0,gp}$	Volumetric flow rate of produced gas (m^3/s)
Q_{mf}	Volumetric flow rate of N_2 at minimum fluidisation velocity (m^3/s)

R	Gas constant (atm.m ³ /mol. K) or (kJ/mol. K)
R'	Number of linearly independent equations
R ²	Coefficient of determination
r _{b,i,j}	Reaction rate of species i in bubble through chemical reaction j (mole/ s m ³)
Re	Reynold number
r _{e,i,j}	Reaction rate of species i in emulsion through chemical reaction j (mole/ s m ³)
r _i	Dense phase overall reaction velocity (reaction rate of species i, mol/s)
R _t	Reaction time per each cycle (s/cycle)
S	Mass percentage of sulfur (dry basis EFB)
s	Source term
T	Temperature
t	Time (s)
t ₁	Characteristic time for pyrolysis
T _F	Temperature of freeboard
U _b	Bubble velocity (m/s)
U _c	Superficial gas velocity at which the pressure curve is maximum (m/s)
U _e	Gas velocity in emulsion (m/s)
U _k	Superficial gas velocity at which the pressure curve is levelled off (m/s)
U _{mb}	Minimum bubbling velocity (m/s)
U _{mf}	Minimum fluidisation velocity (m/s)
U _{ms}	Minimum slugging velocity (m/s)

U_o	Superficial velocity (m/s)
U_{tr}	Transport velocity (m/s)
V	Volume of freeboard (m^3)
V_e	Total volume in emulsion m^3
V_i	Partial gas volume (m^3)
$v_{i,j}$	Stoichiometric coefficient of species i through chemical reaction j
V_j	Gas volume at each sampling step (mL)
v_k	Stoichiometric coefficient of product (k)
V_p	Average pore volume (cm^3/g)
V_T	Total gas volume (mL)
W_1	Mass of carbon (g) (dry basis)
W_2	Mass of hydrogen (g) (dry basis)
W_3	Mass of nitrogen (g) (dry basis)
W_4	Mass of sulfur (g) (dry basis)
W_5	Mass of oxygen (g) (dry basis)
W_c	Mass of catalyst (kg)
W_{EFB}	Mass of EFB (g)
W_f	Mass of fluid
W_h	Watt-hour
W_{H_2O}	Mass of water (g)
W_i	Individual gas species mass (g)
W_{j^T}	Total weight of gases at each time step
$w_{N_2,ca}$	Mass of nitrogen carrier gas required per 1 kg EFB (kg/kg EFB)

W_p	Mass of particle
W_s	Solid mass of fixed carbon / cell volume
W_{sand}	Mass of sand (g)
W_T	Total mass of sand and EFB (g)
$W_{vol}(t)$	Mass of gas components released at each sampling time
$W_{vol,0}$	Mass of the initial volatiles content of EFB
x'	1/temperature
x_1	Mass fraction of biomass
x_{1char}	Mass fraction of char (dry -fuel basis)
x_{2ash}	Mass fraction of ash (dry -fuel basis)
$x_{C,e}$	Mass fraction of char in emulsion phase
x_{char}	Mass fraction of char (ash-free basis)
x_{EFB}	Mass fractions of EFB
x_f	Mass fraction of fluid
$x_{i,EFB}$	Mass fractions of EFB constituents on dry basis
x°	Number of hydrogen atoms in tar chemical formula
x_p	Mass fraction of particles
x_{sand}	Mass fractions of sand
y	Gas mole fraction
y_1	Natural logarithm of rate constant
Y_i	Individual gas species yield (g_{gas} / g_{daf})
$Y_{i,dev.}$	Yield of species from devolatilisation (kg/kg EFB)
$Y_{i,gp}$	Yield of CH ₄ , bio-oil, and tar deducted from the produced gas (kg/kg EFB)

y_{N_2}	Percentage of N_2 in air
y_{O_2}	Percentage of O_2 in air
Y_p	Yield of species in pyrolysis
Z	Bed height (cm)
α_b	Fraction of bed in bubble phase
α_f	Relaxation Factor
α_{mf}	Voidage at minimum fluidisation velocity
ϵ_b	Fraction of bed in emulsion phase
ϵ_p	Particle porosity
θ_p	Particle volume fraction
μ	Dynamic viscosity (N.s/m ²)
μ°	Vector of species chemical potential
ρ_1	Density of biomass (kg/m ³)
ρ_{air}	Density of air (kg/m ³)
ρ_{app}	Apparent density of EFB (g/cm ³)
ρ_c	Density of char (kg/m ³)
ρ_{pe}	Effective density (kg/m ³)
ρ_{sand}	True density of sand (kg/m ³)
σ_{AB}	Constant in the Lennard-Jones potential energy equation function (A ^o)
τ	Residence time (s)
τ_s	Space time (kg h/ m ³)
ϕ_s	Sphericity
Ω_{AB}	Collision integral

CHAPTER 1

INTRODUCTION

1.1 Background

Gasification is a process of producing valuable products such as gases and oil from carbonaceous wastes, and biomass is one of them. This process occurs in environments with deficient in oxygen and requires heat, while combustion needs a sufficient amount of oxygen to take place and releases heat. Different mediums such as air, oxygen, steam and carbon dioxide are used in this process, and these mediums are called gasification agents. The main purpose of this process is to produce useful gases such as H₂, CO, CO₂, CH₄ and light hydrocarbons. Many parameters affect the yield of these gases: temperature and type of gasification agents. These gases can be used in downstream facilities as a fuel to produce heat, electricity, and the like.

Thomas Shirley first attempted to realise gasification in 1659, doing experiments with methane, formally so-called carbureted hydrogen. After that, in Britain, the awareness of using by-product gas accompanied the pyrolysis of coal increased, especially because of overuse of wood and the need to light the streets. However, in 1733 scientists still did not believe in coal-gas as a beneficial source of energy. The period of time from 1798–1802 witnessed a great development in the use of this gas, however, especially after William Murdoch used to light the main building of the Soho Foundry, followed by his astonishing presentation of gas lighting. Meanwhile, in 1804, a coal-gas lighting patent was awarded to a German, Friedrich Winzer.

In its history, the gasification process has experienced major developments in order to compensate for the shortage in fossil fuels, as happened in the Second World War (Basu, 2010). Nowadays, the potential energy demands and consumption have increased worldwide. According to the International Energy Agency (IEA) (International Energy Agency, 2015), the estimates of total primary energy supply (TPES) in 2013 reached 1.575×10^{17} Wh (watt-hour). The main source of energy was coal for the period between 2000 and 2012 followed by oil and natural gas. Also, the hydropower and renewable energy contributed in the total energy consumption (British Petroleum Global, 2018; United Nations & World Energy Council, 2018). Along with increasing the energy demands, the global warming emissions also increased which eventually raise the global temperature. To keep the global temperature increase around 2°C required decreasing 75% of carbon emissions by 2050 (Azar & Lindgren, 2018).

The attention and plans toward production renewable energy have increased significantly, especially in the countries of high biomass production. In South East Asia's countries, the resulted wastes are mainly from the industries of palm oil. In 2014, Malaysia processed 95.38 Mt (million tonnes) of fresh fruit bunch (FFB) of which the

empty fruit bunch (EFB), mesocarp fibre (MF), palm kernel shell (PKS), and palm oil mill effluent (POME) were 7.34, 7.72, 4.46, and 63.9 Mt, respectively (Malaysia Biomass Industries Confederation, 2017). According to this, tar issues arise when demand on syngas production increase. The tar is a main nuisance in thermal conversion processes such as gasification and pyrolysis which is unavoidable byproduct.

This complex product can be defined as a condensable organic mixture which mainly consist of oxygenated hydrocarbons, typically containing single-ring to five-ring aromatic hydrocarbons.

The tar components can be distinguished through splitting the tar into four classes according to the temperature and residence time as the main criteria for the classification (Evans & Milne, 1987). Class 1 comprises the products of the primary pyrolysis, essentially cellulose-derived products, which is released at low temperature (500 °C) (Gómez-Barea & Leckner, 2010). This class consist of acetol, guaiacol, acetic acid, and anisole (Morf, 2001). Class 2, produced in the range (500– 1000 °C), and mainly comprises phenolics and olefins. Class 3 consist of alkyl tertiary products (methyl derivatives of aromatics, such as toluene and indene), formed between 650 and 1000 °C. Class 4 is for the aromatic compounds without substituents such as benzene, naphthalene, anthracene and pyrene, which formed above 750 °C (Gómez-Barea & Leckner, 2010). At severe gasification conditions (very high temperature), the tar converts to refractory tar which hard to destroy compared to primary and secondary tars due to polymerization reactions tendency increase (Srinivas et al., 2013). Therefore, the reduction of tar concentration in the syngas is an essential goal for production of clean energy.

The advantages of using clean energy comprise decreasing the emissions of greenhouse gas resulted from burning fossil fuels, and enhancing the economic through lowering the dependency on a specific type of energy supply. Thus, design and engineering of specialized processing units such as gasification for syngas production, and pyrolysis for bio-oil or char production became among priorities of biomass producing countries. Basically, major modifications on gasification was according to preliminary studies by means of mathematical models or specialised simulation programs.

The gasification modelling has become one of the basic activities for studying and developing this process and other related ones, such as pyrolysis and combustion. Nowadays, most important companies and institutions around the world adopt and use this activity. In addition, it has often been the main focus of conferences and symposia. The criteria applied in the modelling of this process is in optimizing synthesis gas production, understanding the complex behaviour of gasification, reducing tar yield, and estimating the power produced from the biomass integrated gasification combined cycle (BIGCC).

1.2 Problem Statement

Tar is a problematic side product formed during devolatilisation of biomass at temperature range (300– 500°C). It is a black, thick, highly viscous, wide-range hydrocarbons mixture condense in colder parts of the unit. Ambitious utilization of syngas affected by the high concentration of tar. In particular, tar formation can cause blocking in downstream equipments such as gas coolers, filter elements, pipes, valves, heat exchangers and engine suction channels, and cause catalyst deactivation. Moreover, adherence problems appear on turbine blades, and tar also considered as a corrosive material. As a result, the total efficiency is decreased and the cost of the process is increased.

Hence, it is substantial to estimate the tar levels (or concentration) before using syngas as a fuel in internal combustion engine (ICE) which has tolerance for tar. The target concentration of tar for fuel applications is below 5 mg/m³ (Srinivas et al., 2013). Despite tar concentration in the syngas is a crucial issue for downstream utilization, its influence on the mass balance is insignificant. However, the influence of tar concentration is more evident on the heat balance because of its high energy density. In general, gasification unit comprises four stages take place simultaneously: drying, devolatilisation (or pyrolysis), gasification, and combustion. The tar formed during devolatilisation stage can experience secondary reactions in the vapour phase (homogenous) such as thermal cracking. Hence, more realistic devolatilisation model coupled with kinetic of the secondary reactions is required to describe the decomposition of EFB.

Due to complexities of devolatilisation mechanism which consist of many non-elementary reactions, equilibrium model (EM) is adopted in many published works for preliminary estimation of gas composition. This model assumes that equilibrium is reached in the outlet streams since the devolatilisation takes place rapidly. At equilibrium, the system attained more stable composition when its Gibbs free energy is minimized. In fact, the equilibrium is not achieved under practical conditions due to low temperature used in fluidised-bed gasifier between 700 and 900 °C, where extreme conditions required for water-gas shift reaction (WGSR) to reach equilibrium (above 1000 °C). As a result, EM predicts gas composition free of CH₄, tar, and char. In addition, the model overestimates the yields of H₂ and CO, and underestimate the yield of CO₂ (Gómez-Barea & Leckner, 2010). The formation and destruction of tar are not predictable using EM as well (Srinivas et al., 2013).

To sum up, the aim of EM is to predict the maximum composition of devolatilisation products. Moreover, high temperature and long enough residence time are required for the proper application of EM (Gómez-Barea & Leckner, 2010). On the other hand, many studies of gasification unit use the kinetic approach of individual gas species to compute the gas composition released from devolatilisation, neglecting the interaction of the bulk gas. This interaction mainly occurs through WGSR and among the species (H₂, CO, CO₂, and H₂O), where the produced composition is considered as an input for gasification stage. The chemistry of tar destruction affected by kinetic and equilibrium reactions

which represented by thermal decomposition of tar and WGSR, respectively (Simell et al., 1997).

Regarding tar modelling, some works model the tar using an empirical formula ($C_kH_lO_m$) which estimates the composition of tar based on three atoms (carbon, hydrogen, and oxygen). In other words, the type of tar (primary, secondary, and tertiary) which is classified according to its formation temperature and residence time is not explicitly represented, but it is lumped. In fact, the tar is very reactive substance and can change its composition from oxygenated to multi-aromatic compounds depending on the operating conditions of the gasification process. Moreover, modelling the tar as hydrocarbon compounds other than CH_4 are not thermodynamically stable. In other words, these hydrocarbons in EM can considered not thermodynamically favourable species (Yan et al., 2005).

Unlike equilibrium calculations, pseudo-equilibrium model (PEM) has better results compared to EM. It improves the predictions through inclusion empirical relations and kinetic models of kinetically limited-conversion products such as tar, bio-oil, and CH_4 as well as correction factor for WGSR deviation from equilibrium. Moreover, this model allows to solid carbon, tar, and CH_4 to be included in the outlet stream. The model is capable to capture the changes in the operating conditions of devolatilisation such as temperature and carrier gas flow rate. The model is capable to estimate the carbon and WGSR conversions as part of the model rather than being as inputs.

Mixing is one of the significant issues in fluidised-bed reactors, especially for top feeding reactors where different products distribution obtained (Corella et al., 1988). In fact, the carbon and tar conversion depend on the location of the feed point. The closer feed point to the air inlet result in maximum conversion of carbon due to high consumption of O_2 (Goyal et al., 2010). In addition, there is a considerable difference between feeding at the top or the bottom of the gasifier unit. In the latter case, pyrolysis products pass through whole bed which provide good mixing and reduce tar content. As a result, the yield of the permanent gases increase due to tar cracking in the hot bed (Radmanesh et al., 2006). In other words, the movement of solid and gas in the bed and freeboard greatly affects the efficiency of carbon conversion and tar content of the gas (Gómez-Barea & Leckner, 2010). Many studies in literature modelled the fluidised-bed using two-phase theory which assumes perfect mixing of solid in emulsion phase since the modeled reactors are bottom feeding. However, in case of top feeding, the fuel particles are of different shapes and physical properties from the inert bed material (sand) which tend to float on the top of the bed during the devolatilisation due to jet release of the volatiles (Gómez-Barea & Leckner, 2010). The produced char from the devolatilisation sinks into the bed, where meets the hot air. Thus, a significant percentage of O_2 may be exhausted because of combustion reactions take place to some extent. The use of an equation describing the diffusion of char inside the bed is essential to estimate the conversion of carbon and consumption of O_2 during this stage.

1.3 Scope of Work

The purpose of this work is to model uncatalyzed tar cracking (thermal cracking) taking place in a lab-scale gasifier. This gasifier is a bubbling fluidised-bed reactor of dimensions (inside diameter = 40 mm; height = 600 mm), using EFB as the biomass source. The complexity of the fluidised-bed reactor comprises a considerable number of interactions take place simultaneously among chemical and physical processes. As a consequence, obtaining a reasonable and tractable model requires simplifications. The useful approach for simplification in modelling a fluidised-bed gasifier (FBG) is based on identification of rate-determining processes. In other words, it means to distinguish between transport (movement by convection and dispersion) and conversion processes according to their time difference. Three conversion processes occur inside the FBG with different rates: devolatilisation, char combustion, and char gasification.

Devolatilisation has faster rates compared to the gasification and combustion of char, which is distinguished to be the first stage takes place in the gasification unit. Thus, the devolatilisation of the EFB was modelled to occur upon the entry of the reactor. In fact, the EFB is very reactive under high thermal conditions because of high volatile matter content which reaches around 83 wt% (Mohammed, 2011), and small particles size used in this research with average diameter of 0.4 mm (obtained in this study). Compared to mixing rates inside the FBG, the devolatilisation is faster than mixing, this especially holds for narrow lab-scale FBG, as reported by Gómez-Barea and Leckner (2010). Hence, the completion of the devolatilisation proceeds in the freeboard (FB) of the FBG, and separated from the fluidised sand bed. Moreover, the produced gas and vapours from this stage leave the FB due to small residence time compared to char reactions. In other words, the gasifying agent can not reach the char because of slow rates of diffusion. Therefore, the bulk gas from the devolatilisation do not interact with the products of char gasification reactions (Kaushal et al., 2010).

The PEM was applied to model the devolatilisation of the EFB in a top-feeding fluidised-bed reactor. For that purpose, an experimental work conducted for EFB devolatilisation in a fluidised-bed reactor at high temperatures (650– 850 °C). Due to system limitations, an increment of 100 °C was used. The devolatilisation experiments carried out at this range because much higher EFB decomposition obtained than that which would be at low temperatures. In other words, primary decomposition and secondary reactions (represented by tar vapours cracking) tend to occur simultaneously. Particularly, tar cracking reactions take place at temperatures higher than 600 °C (Fagbemi et al., 2001). Moreover, the devolatilisation represents the first stage in each gasification units which normally operate at this range. Consequently, the final gas yield is higher compared to low temperatures. The aim of the experiments is to obtain empirical relations between the yield of devolatilisation products (H_2 , CO, CO_2 , CH_4 , bio-oil, tar, and char) and temperature. In addition, the kinetic parameters for both the primary and secondary reactions lumped in a global mechanism and estimated. These parameters along with empirical relations considered as inputs required for PEM.

The liquid bio-oil was also considered in the PEM due to its importance as an energy carrier resulted from the decomposition of lignocellulosic biomass such as EFB (Becidan et al., 2007). In fact, the bio-oil is a complex organic mixture of low and high molecular weight oxygenated compounds (Kaushal & Abedi, 2010). Moreover, the bio-oil has high energy density and maximum yield of 42% obtained from EFB pyrolysis at 500 °C, which undergoes further cracking at higher temperatures (Chang, 2014; Mantilla et al., 2014). The criteria of the PEM represented by deduction the atoms of carbon, hydrogen, and oxygen from the yield of unconverted tar, bio-oil, and CH₄.

Kinetic models for the tar and bio-oil cracking as well as steam reforming of CH₄ were adapted from literature. A plug-flow reactor was used to evaluate the conversion of the tar, bio-oil, and CH₄ in the FB section of the reactor. The deviation of WGSR from equilibrium was estimated using a correction factor (f_{WGSR}). This factor equals to the ratio of the experimental (K_{exp}) and the theoretical equilibrium constants (K_{WGSR}). Later, solving the atomic balance equations for the carbon, hydrogen, and oxygen result in the pseudo-equilibrium composition. Then, the final gas composition was evaluated from the overall material balance. Two component models represented the tar and bio-oil. For tar, toluene (C₇H₈) was chosen because it is a secondary tar evolved at temperature above 650 °C. While, phenol (C₆ H₆ O) is the most abundant component in the bio-oil. Although, the tar and bio-oil have a large number of components, only a few considered in modelling for reasons of simplicity and lack of kinetic data availability. In sum, the model has the capability to capture the variations in process conditions such as temperature and carrier gas flow rate. Moreover, it is applicable to different types of biomass depending on their proximate and ultimate analysis.

For the bottom part of the reactor, the produced char from the previous stage (devolatilisation) tends to sink inside the FBG. This part was modelled according to the two-phase theory of fluidisation for estimation of carbon conversion and oxygen consumption, where the bed is divided into two phases, representing the bubble and emulsion. The bubble phase comprises only gas-gas reactions, while gas-solid and gas-gas reactions occur in the emulsion. The gasification and combustion reactions of char were modelled according to their speed of reaction. In fact, the combustion of char is the fastest among char reactions.

Particularly, the gasification reaction of char (char-carbon dioxide reaction) is six to seven orders of magnitude slower than combustion (Basu, 2010). Therefore, the combustion reactions were modelled in a separate sub-model, considering the evolution of char inside the bed. The outputs of this model representing the inputs for the gasification reactions sub-model, where the gasification reactions take place together with char mixing. Hence, kinetic reactions equations were adapted from literature as a function of char mass fraction along bed height. Semi-empirical fluid-dynamic correlations were used to estimate gas-flow parameters. For instance, bubble velocity, minimum fluidisation velocity, bubble size, and bed voidage at minimum fluidisation velocity are very important in fluidisation systems. Despite the empirical nature of the flow-dynamics, the fluidisation model (FM) has been applied successively and widely for modelling FBG.

1.4 Research Objectives

The main goal of this research is to build a model that predicts tar yield and its conversion from a bench-scale fluidised-bed reactor, applied as a gasifier that uses EFB as a feedstock under different conditions. The specific objectives are as follows:

- i. to evaluate the physical properties of EFB, char, and sand, and thermal behaviour of EFB through estimating the kinetic parameters of the devolatilisation stage on a bench-scale fluidised-bed reactor at different temperatures;
- ii. to estimate the tar yield and its conversion as well as bio-oil, char, and gaseous products (H_2 , CO , CO_2 , CH_4 , and N_2) resulted from the devolatilisation stage using pseudo-equilibrium model;
- iii. to estimate carbon conversion and O_2 consumption in gasification stage using two-phase model;
- iv. to investigate the effects of temperature and carrier gas on the yield of tar and remaining devolatilisation products, and the effects of temperature and equivalence ratio (ER) on the yield of gasification sub-model.

1.5 Thesis Layout

The layout of the thesis includes the following chapters:

Chapter 1 presents the introduction, problem statement, research objectives, scope of the research, and thesis layout.

Chapter 2 discusses oil palm as an energy source, the main constituents and thermal behaviour of lignocellulosic biomass, the thermal processes of biomass, the principles of chemical equilibrium and kinetic, types of gasifiers, fluidised-bed reactors and fluidisation regimes, segregation behaviour in fluidised bed reactors, Geldart's classification of particles, gasification models, and biomass tar.

Chapter 3 details the research methodology, including the materials, experimental procedure and setup, characterisation of fuel and bed material, products recovery and analysis, devolatilisation sub-model assumptions and equations, combustion sub-model equations, gasification sub-model assumptions and equations, and hydrodynamic model assumptions.

Chapter 4 presents the method of characterisation of physical properties for both EFB and sand. Further discusses the experimental work results, and shows the yield correlations for species.

Chapter 5 reveals the results of devolatilisation sub-model and validates with the experimental work (this study) on the same system.

Chapter 6 presents the effects of char mixing on carbon conversion and O₂ consumption through applying sub-models for the combustion and gasification which consist of combustion and gasification reactions, respectively.

Chapter 7 is about testing the aforementioned sub-models response (devolatilisation, gasification, and combustion) by changing each process parameter.

Finally, Chapter 8 offers the thesis's conclusions and recommendations for future work.

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PUBLICATION

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