MODEL DEVELOPMENT OF TAR CRACKING FOR BIOMASS STEAM GASIFICATION FOR HYDROGEN PRODUCTION

by

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16059

Dissertation report submitted in partial fulfilment of

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Chemical

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CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL)

Approved by,

____

(DR. ABRAR INAYAT)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

KEVIN KAN SHIU KWANG

ABSTRACT

Hydrogen production from biomass gasification has become an alternative source of energy replacing combustion of fossil fuels. However, biomass steam gasification not only produces useful products but unwanted products such as tar that will affect the efficiency of the gasification utility. Therefore, various methods to eliminate tar into other useful products have been carried out. This research project focuses on the development of kinetic reaction model of tar cracking based on steam gasification by using simulation software such as MATLAB and to calculate the reaction constant of tar cracking via optimization approach.

ACKNOWLEDGEMENT

First and foremost, I would like to express my utmost gratitude to my Final Year Project's supervisor, Dr Abrar Inayat for his guidance, supervision, encouragement and support throughout my final year project period. Dr Abrar has provide many knowledge on how tar cracking is being developed as well as his teaching on using MATLAB to develop kinetic model for my final year project. Without his guidance and assistance this project may not be smooth or able to complete on time.

Appreciation and gratitude also goes to Dr Sintayehu Mekuria Hailegiorgis (coordinator for Final Year Project I Sept 2014 semester) and Dr Asna bt. Mohd Zain (coordinator for Final Year Project II, Jan 2015 semester) for successfully coordinate this course for us. Without their effort, this project may not be able to be conducted.

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ABBREVIATION AND NOMENCLATURE

CO : Carbon Monoxide

CO_2 : Carbon Dioxide

H_2 : Hydrogen

H_2O : Water

k : Kinetic Rate Constant

A : Arrhenius Constant

E_a : Activation Energy

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

Presently, the major source of energy in the world is heavily dependent on finite fossil fuels which are not a type of renewable energy. According to World Development Indicators (The World Bank, 2011) in the year of 2011, 81.5% of total energy uses in the world are generated from fossil fuels, followed by 9.8% from combustible renewable and waste and 8.7% from other alternative such as nuclear energy. In years to come, the amounts of fossil fuels will slowly decreasing and eventually extinct causing a serious energy crisis worldwide. The combustion of fossil fuel for power generation poses unresolved impact on the climate. With the existence of these two problems creates an urge to explore and find an alternative of energy production with a better, environmental-friendly, and renewable source(s).

Solar and wind powered energy generation are one of the renewable energy that are most promising for replacing fossil fuel-based energy generation. However, these energy generations are site-dependent, weather-dependent, and inconsistent which caused it to be unreliable for continuous supply of energy. That means solar and wind energy generation could be used as a backup energy generation but not as a main energy generation to replace energy generation by fossil-fuel combustion.

Fossil fuels generally are fuels formed by natural processes such as decomposition of buried organism on earth which aged over millions of years. These fuels contain high percentage of Carbon composition with inclusive of coal, petroleum and natural gas. Fossil fuels have a wide range of materials such as volatile materials with ratio close to hydrocarbon, like methane, CH_4, to non-volatile materials with close to pure Carbon compound.

Combustion of fossil fuels for vehicle transportation and stationary power generation will emit polluting gaseous and particulates that can cause harm to the environment across the globe. These combustions with ambient air emit gaseous known as flue gas. Majority of the flue gas are made up of un-combusted nitrogen, followed by Carbon Dioxide (CO_2) and water vapour which created by the combustion of Hydrogen in the fuel with the atmospheric oxygen. A typical flue gas also contains very small amount of Nitrogen Oxides (NO_x) and Sulphur Dioxide

(SO_2) which are harmful to the environment as there are presences of Nitrogen and Sulphur in some fossil fuels. Increased in these pollutant into the atmosphere could lead to global warming throughout the mother earth, giving pressure and stress to researches to come out with an alternative source of energy that are less harmful or environmental-friendly.

With the use of battery energy storage, capacity of the storage is limited and it will only be a temporary solution of energy supply but not as a long term solution. Hydrogen energy production has been identified as a potential alternative fuel and energy carrier for future energy supply. Theoretically, hydrogen is clean and it can be produced from water which is available in a very large quantity on our mother earth. With the aid of fuel cell, when hydrogen is converted into useful electricity, the by-product of the process is an environmental friendly component, water.

Hydrogen is mainly produced from combustion of fossil fuels such as natural gas steam reforming. However, this process is non-renewable and non-environmental friendly as the by-product of this process is a pollutant to the environment. A study has been conducted on alternative ways of hydrogen production by using renewable sources. Many scientists believe that the development of renewable energy can effectively eliminate the current problem of global warming. Global warming effects and energy supplies issues have been drawn more attentions from all around the world. In recent years, the use of bio-energy is increasing as a new source of renewable energy and has the potential on replacing energy generation from fossil fuels.

One of the potential renewable energy sources to generate energy is coming from biomass (Tanksale et al., 2010). Biomass could be converted into heat electricity, several types of fuels such as solid, liquid and gas fuels which includes hydrogen and synthetic gas. Gasification refers to an oxidation process converting carbon sources mainly biomass, coal or natural gas into possibly hydrocarbon molecules as well as other side products such as Carbon Monoxide (CO), Hydrogen (H_2) or Carbon Dioxide (CO_2).

1.2 PROBLEM STATEMENT

The production of synthetic gas and hydrogen from gasification process is one of the most promising options for utilizing biomass. The syngas that produced from biomass can be used to generate power by using gas turbines as well as converting into chemical products such as methanol, dimethyl-ether through catalyst.

However, biomass steam gasification not only produces useful products such as Hydrogen (H_2), many by-products are also formed during the process such as fly ash, NO_x, Sulphur Dioxide (SO_2) and tar. Tar is an unwanted constituent of producer gas from biomass gasification that could cause severe operating problems in the process equipment such as filters, engines, turbines and fuel lines due to condensation occurred as temperature is lower than its dew point. Tar is a complex mixture of condensable hydrocarbons which includes single ring to five-ring aromatic compounds along with other oxygen containing hydrocarbon or complex polycyclic aromatic hydrocarbons.

Milne et al (1998) tabulated the tolerance limit of tar for various end use devices suggested by different researchers. The preferable tar and dust loads in gases for engines is recommended to be lower than 10 mg/m^3 as mentioned by Bui et al (1994).

Various research methods on tar cracking had been carried out by many researchers or scientist. Han & Kim (2008) had reviewed past literature on some of the possible methods on tar cracking and summarized each method into five groups mainly mechanism method, self-modification methods, thermal cracking, catalyst cracking and plasma method.

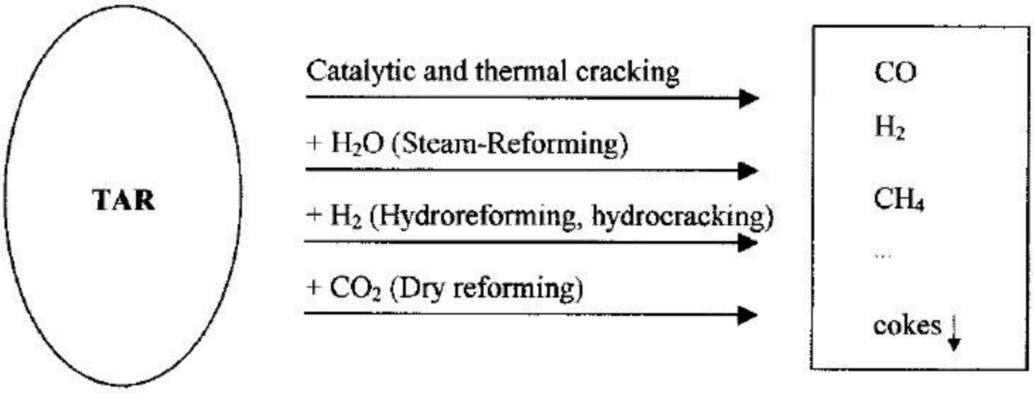


Figure 1: Summary of tar elimination method to produce useful products.Adapted from “Improving the Modelling of Kinetics of Catalytic Tar Elimination” by Corella, 2002

1.2 OBJECTIVE

The objective of this research study is:

1. To develop a reaction kinetic model for tar cracking based on steam gasification
2. To calculate the reaction constants of tar cracking by using optimization approach.

1.3 SCOPE OF STUDY

The scope of study in this research focuses on the reaction kinetic modelling development of tar cracking for biomass steam gasification for Hydrogen (H_2) production in order to understand the kinetic reactions of tar cracking to prevent problems that occurred due to the presence of tar in the reactor and thus prolonging the operating time of the reactor for Hydrogen production. On the other hand, this research project also calculates the reaction constant of tar cracking by using optimization approach to optimize the utility system of tar cracking to enhance the production of Hydrogen most economically.

2.0 LITERATURE REVIEW

The removal of tar by thermal cracking and partial oxidation are highly dependent on the temperature and the residence time of the gases. According to Brandt & Henriksen (2000), to achieve a sufficiently high tar cracking efficiency from thermal cracking, the necessary temperature and residence time are 1250^{o}C and 0.5 seconds respectively.

In the past literature, tar was reduced by thermal cracking by using fluidized bed gasifier (Bridgwater, 1995). Bridgwater also mentioned that biomass-derived tar was refractory and thermal treatment alone is not sufficient to be crack. Therefore several methods has been suggested by the author such as increasing residence time by using a fluidized bed reactor freeboard to further enhance the tar cracking. However, this method appears to be only partially effective as a significant energy supply is required for the independently heated hot surface contact and decrease in the overall efficiency.

Houben (2003) has conducted another thermal cracking experiment with the temperature range of 900-1150^{o}C and residence time ranging between 1 and 12 seconds. From the results obtained by Houben shows that the concentration of tar decreases exponentially as the residence time and operating temperature increases exceeding 900^{o}C as shown in Figure 1 below. The mean value of total tar concentration initially is approximately 8g/Nm^3 with the standard deviation of 0.85. The raise in temperature at 1150^{o}C well as residence time of 4 seconds able to reduce the tar concentration from 8g/Nm^3 to 0.2g/Nm^3.

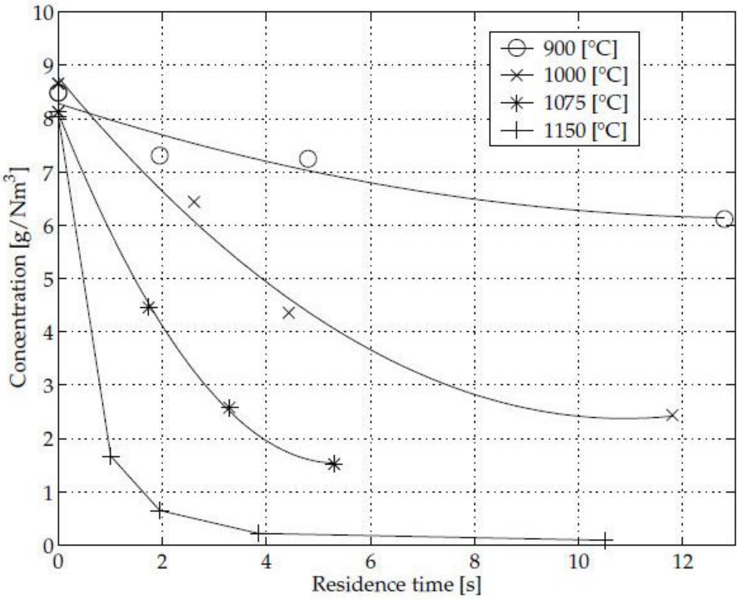


Figure 2: Tar concentration as a function of residence time graph. Adapted from Analysis of tar removal in a partial oxidation burner (p. 63) by Houben, 2003

Houben had conducted another experiment that studies the effect of temperature in the reactor on production of gas. Figure 2 shows the composition of gas (in terms of mole %) against residence time at the operating temperature of 1150°C.

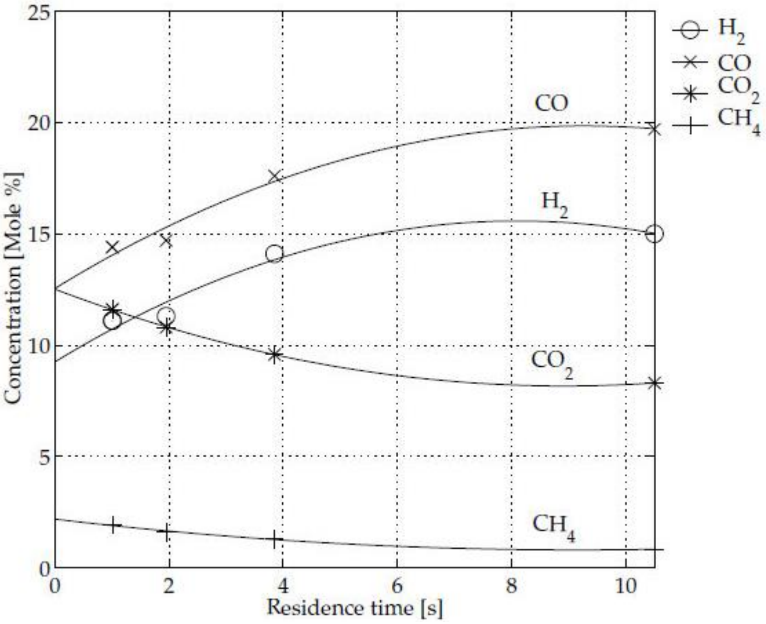


Figure 3: Graph of concentration of gas product against residence time at 1150°C. Adapted from Analysis of tar removal in a partial oxidation burner (p. 63) by Houben, 2003

From the results obtained by Houben, it can be said that the amount of gas composition can be influenced by the residence time in the reactor. The composition of Carbon Monoxide and Hydrogen shows an increase in composition as residence time increases whereas Carbon Dioxide and Methane shows a decrease in composition.

Morf et al (2002) has conducted an experiment to investigate homogeneous tar conversion without the external supply of oxidants in a tubular flow reator operated at temperature ranging from 500 to 1000^{o}C with residence time below 0.2 seconds. From the results obtained by Morf et al under the specified reaction condition, the increase in concentration of Carbon Monoxide, Hydrogen and Methane in the pyrolysis is indicated when the temperature of homogeneous secondary tar reaction exceeds more than 650^{o}C. the highest conversion that Morf et al manage to obtain in the experiment is 88% at a reference reaction temperature of 990^{o}C and isothermal residence time of 0.12 seconds.

Evans and Milne (1987) has characterized the types of tar compounds based on the temperature range. The primary products of tar cracking found in the reactor are ranged between the temperature of 400-700^{o}C with the presence of oxygenated compounds. The secondary products formation temperature are usually ranging from 700-850^{O}C which includes phenolics and olefins. The aromatics which is classified as tertiary products are in the reaction range of 850-1000^{O}C and could further be subdivided into classes of "alkyl tertiary products".

According to Devi et al (2003), the high Hydrogen production during steam gasification can be attributed by the following chemical equations that represents tar reforming reaction which contributes to increment in the content of Hydrogen and CO gases.

$$C_nH_x + nH_2O \rightarrow \left(n + \frac{x}{2}\right) H_2 + nCO$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

$$C + H_2O \rightleftharpoons H_2 + CO$$

The presence of Carbon Dioxide in the atmosphere will cause the use of it as gasifying medium to be promising. Tar reduction is also enhanced by dry reforming reactions of Carbon Dioxide. Minkova et al (2000) states that a mixture of steam-CO_2 gives the highest degree of carbonization in a rotating reactor for gasification of biomass. This mixture also produces large activity char, resulting to high ash content. CO_2 gasification in the presence of catalyst converts tars and decrease of the amount of Methans and C_2-fraction as well as increasing the Hydrogen and Carbon Monoxide yields. The significant decrease in Carbon Dioxide content was observed with CO_2/Biomass ratio of 1:16 indicating Carbon Dioxide converts into other products. The main chemical reaction equation with Carbon Dioxide as gasifying medium that represents drt reforming reaction of tar is as below.

$$C_nH_x + nCO_2 \rightarrow \left(\frac{x}{2}\right) H_2 + 2nCO$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$CO_2 + C \rightleftharpoons 2CO$$

Generally, Li &Suzuki (2009) had summarized the tar decompositions by various methods into equations as shown below:

a. Thermal cracking $pC_nH_x \rightarrow qC_mH_y + rH_2$

b. Steam reforming $C_nH_x + nH_2O \rightarrow \left(n + \frac{x}{2}\right) H_2 + nCO$

c. Dry reforming $C_nH_x + nCO_2 \rightarrow \frac{x}{2} H_2 + 2nCO$

d. Carbon formation $C_nH_x \rightarrow \frac{x}{2} H_2 + nC$

C_nH_x represents tar and C_mH_y represents to smaller hydrocarbon than tar

The overall rate of tar cracking into smaller hydrocarbons is given by the sum of the rates of all the elementary individual reactions that involved in the network of tar cracking. The first order kinetic reaction has been accepted by many institutions worldwide that is working on biomass gasification. Corella et al. (2002) summarized the overall rate equation into:

$$-r_{tar} = kC_{tar} + k'y_{H_2O}C_{tar} + k''y_{H_2}C_{tar} + k'''y_{CO_2}C_{tar}$$

$$= \left(k + k'y_{H_2O} + k''y_{H_2} + k'''y_{CO_2} + \cdots\right)C_{tar}$$

$$= k_{app}C_{tar}$$

3.0 METHODOLOGY

3.1 RESEARCH METHOLODOGY

Past literature has been reviewed as a preliminary research of this research project based on the project title assigned by supervisor. Literature review focuses on various methods of tar cracking that has been studied by scientist and researches. Main reaction of tar cracking also has been reviewed in order to understand the fundamentals of tar cracking as mentioned by Li &Suzuki (2009).

Literature regarding thermal and catalytic tar cracking is then furthered being reviewed to understand the topic. Upon understanding thermal and catalytic tar cracking, reaction kinetic model for tar cracking based on steam gasification is being studied but further research is required to improvise the kinetic reaction modelling as Corella et al. (2002) reviewed that there are some deficiencies present in the model.

Understanding of simulation software such as Aspen HYSIS or MATLAB is required to conduct this project research. The validation or feasibility of the model can be determined by using the simulation software.

This research project also covers the calculation of reaction constant via optimization approach. MATLAB function, fmincon is used in order to solve optimization calculation for respective reaction rate constant.

Experimental result of yields of Carbon Monoxide, Carbon Dioxide and Hydrogen during homogeneous tar conversion obtained by Morf et al. (2002) is used as equation constraint for optimization calculation. Three different temperatures of 600^oC, 700^oC and 800^oC are taken for calculation.

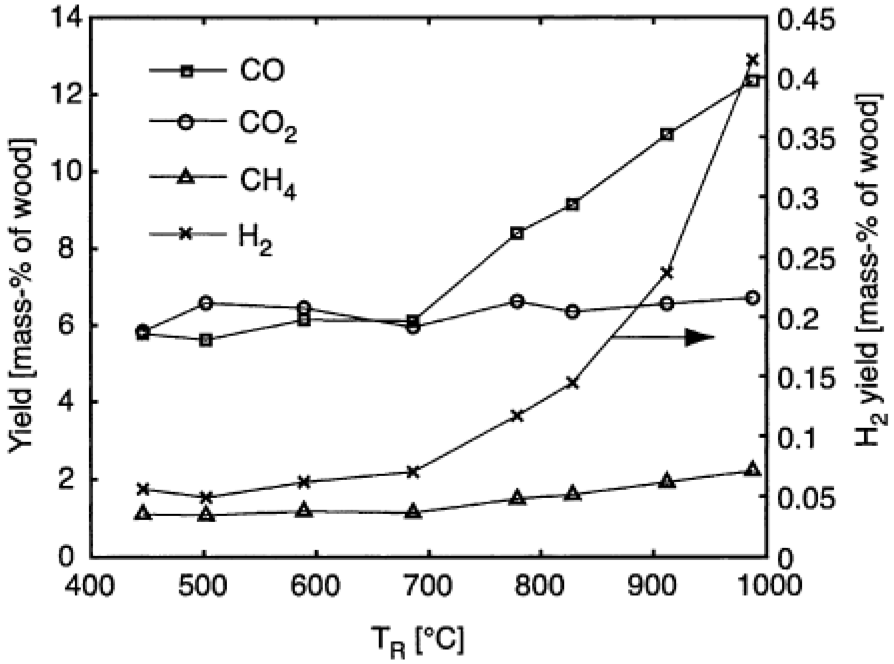
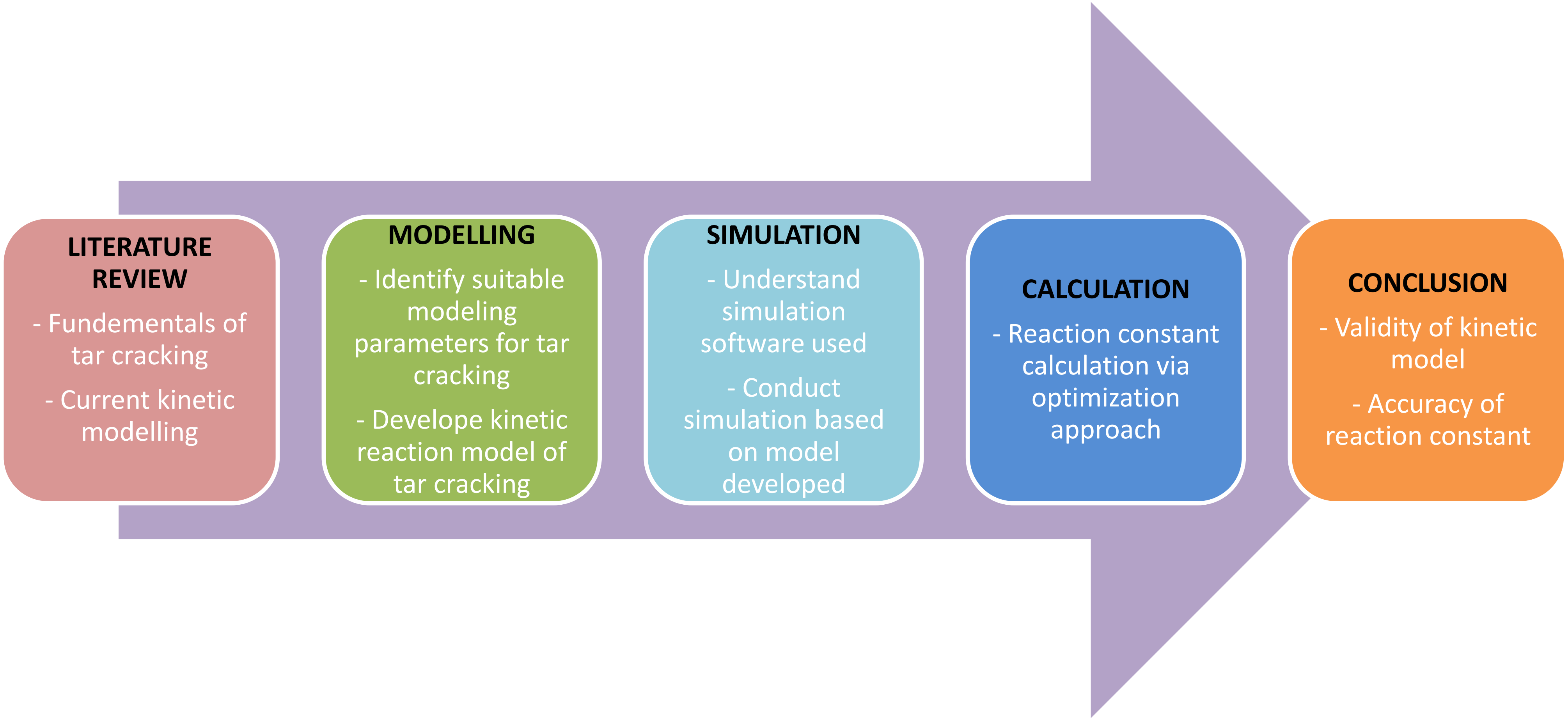


Figure 4: Graph of yields of various components during homogeneous tar conversions at different temperature. Adapted from Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips (p. 847) by Morf, 2002

3.2 PROJECT FLOW CHART FOR FINAL YEAR PROJECT



3.3 GANTT CHART

Activity / Task	Week No													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Continuation of research project	🟦	🟦	🟦	🟦	🟦	🟦								
Submission of draft for progress report						🟦	🟦							
Submission of progress report							🟦							
Preparation for Pre-SEDEX								🟦	🟦	🟦				
Pre-SEDEX evaluation										🟪				
Submission of draft for Final Report											🟪			
Submission of soft bound Dissertation												🟪		
Submission of Technical Paper												🟪		
Viva evaluation													🟪	
Submission of hard bound project dissertation														🟪

🟦 Process

🟪 Suggested Milestone

4.0 RESULTS AND DISCUSSION

Based on the past research literature, the expected results to be obtained from this research project is shown in Figure 4.

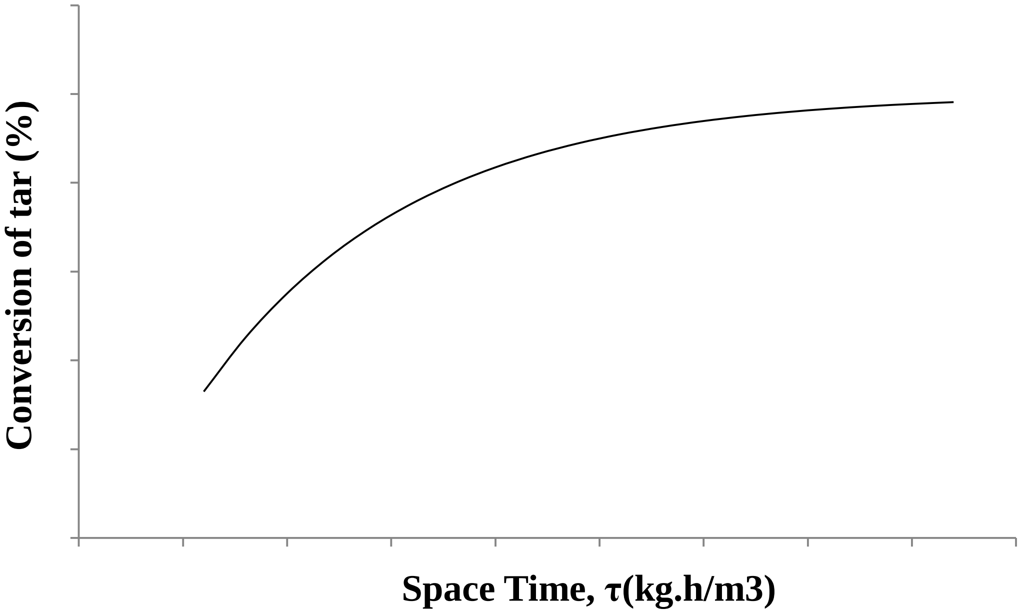


Figure 5: Graph of conversion of tar against space time (expected result)

The value of expected conversion of tar should be increasing as space time increases until it reaches an equilibrium point towards the end.

On the other hand, Figure 5 shows the expected result of the apparent kinetic rate constant, k_{app} in the function of time.

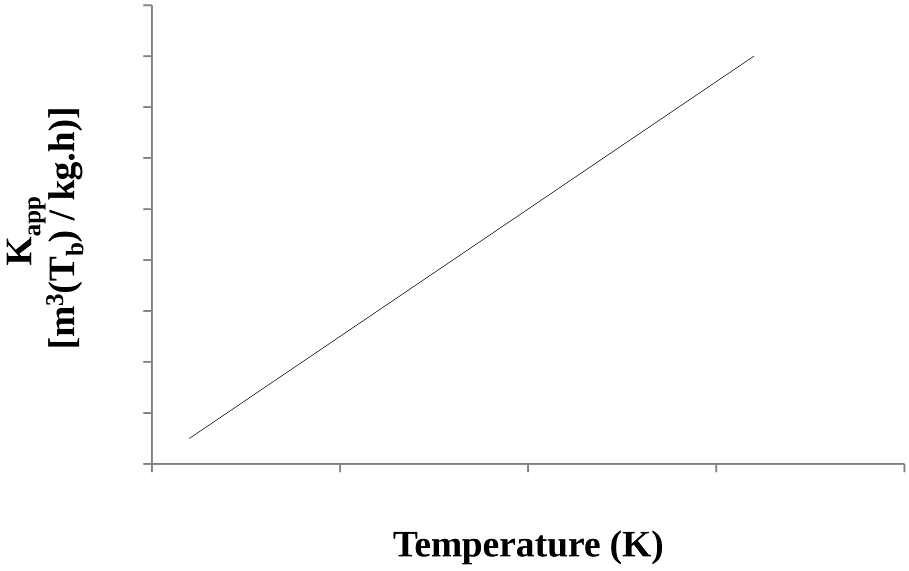


Figure 6: Graph of apparent kinetic rate constant against temperature (expected result)

The apparent kinetic reaction constant is expected to be proportional with the operating temperature. As temperature increases, the reaction constant increases too.

There are many types of heavy hydrocarbon composition that presence in tar. However, based on past literature researchers had carried out decomposition reactions using model biomass tar with compounds such as Benzene, Toluene and Napthalene.

Benzene and Toluene undergoes steam reforming along with homogeneous water-gas shift reaction as shown in the reaction equation (1) to (5)

Benzene:

$$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO \tag{1}$$

$$C_6H_6 + 12H_2O \rightarrow 15H_2 + 6CO_2 \tag{2}$$

Water Gas shift (WGS):

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{3}$$

Toluene:

$$C_7H_8 + 7H_2O \rightarrow 11H_2 + 7CO \tag{4}$$

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2 \tag{5}$$

There are many possibilities for the rate equation that is able to represent the kinetics behaviour of reaction (1) to (5). In this project, the reaction is assumed to be first order reaction with respect to the concentration of the reactant selected by using the formula:

$$r_i = k_i[C_A][C_B]$$

Where r_i : rate of reaction

k_i : kinetic rate constant

C_A/C_B : Concentration of reactant.

Therefore, the rate of reaction for the above reaction (1) to (5) can be summarised to

$$r_1 = k_1[C_6H_6][H_2O]$$

$$r_2 = k_2[C_6H_6][H_2O]$$

$$r_3 = k_3[CO][H_2O]$$

$$r_4 = k_4[C_7H_8][H_2O]$$

$$r_5 = k_5[C_7H_8][H_2O]$$

The overall volumetric rate of each component can be determined according to chemical reactions engineering rules.

$$R_{H_2} = 9r_1 + 15r_2 + r_3 + 15r_4 + 18r_5 \tag{6}$$

$$R_{CO} = 6r_1 - r_3 + 7r_4 \tag{7}$$

$$R_{CO_2} = 6r_2 + r_3 + 7r_5 \tag{8}$$

Total volumetric rate of component obtained is the sum of equation (6) to (9).

$$R_T = R_{H_2} + R_{CO} + R_{CO_2} \tag{10}$$

Volumetric percentage of rate of component can be derived as

$$\%R_{H_2} = \frac{R_{H_2}}{R_T} \times 100\%$$

$$\%R_{CO} = \frac{R_{CO}}{R_T} \times 100\%$$

$$\%R_{CO_2} = \frac{R_{CO_2}}{R_T} \times 100\%$$

4.1 DEVELOPMENT OF MATLAB CODING

Various function file and main file (M-File) is developed for optimization calculation

4.1.1 Function files

a. Rate order calculation

```
function [r] = Calc_rate_1order(T,k,E)

% input (T,k,E)
% T : temperature

%Calculate rate

 r = k*exp(-E/T);
```

b. Product gas component calculation

```
function [RH2 RCO RCO2] = calc_prod_gas_com(r1,r2,r3,r4,r5)

 %Hydrogen
    RH2 = 9*r1 + 15*r2 + r3 + 11*r4 + 18*r5;

%Carbon Monooxide
    RCO = 6*r1 - r3 + 7*r4;

%Carbon Dioxide
    RCO2 = 6*r2 + r3 + 7*r5;
```

c. Reaction kinetics model of tar thermal cracking

```
function [RH2 RCO
RCO2]=run_reaction_kinetics_model_kinetics_parameters(T,A1,E1,A
2,E2,A3,E3,A4,E4,A5,E5)

 %T=TEMPERATURE (K)

global EFB; %EFB feedrate (g/hr)

 %A1 %Benzene thermal for CO/H2(pre-exp factor)
 %E1 %Benzene thermal for CO/H2(E/R)
 %A2 %Benzene thermal for CO2/H2(pre-exp factor)
 %E2 %Benzene thermal for CO2/H2(E/R)
 %A3 %WGS forward reaction(pre-exp factor)
 %E3 %WGS forward reaction(activation energy)(E/R)
 %A4 %Toluene thermal for CO/H2(pre-exp factor)
 %E4 %Toluene thermal for CO/H2(E/R)
 %A5 %Toluene thermal for CO2/H2(pre-exp factor)
 %E5 %Toluene thermal for CO2/H2(E/R)



 %%RECTION KINETICS MODEL%

 % calculate rate for Benzene thermal cracking for CO/H2
[r1]=Calc_rate_1order(T,A1,E1);

 % calculate rate for Benzene thermal cracking for CO2/H2
[r2]=Calc_rate_1order(T,A2,E2);

 % calculate rate for WGS (forward)
[r3]=Calc_rate_1order(T,A3,E3);

 % calculate rate for Toluene thermal cracking for CO/H2
[r4]=Calc_rate_1order(T,A4,E4);

 % calculate rate for Toluene thermal cracking for CO2/H2
[r5] = Calc_rate_1order(T,A5,E5);

 % calculate product gas copmpsition
[RH2 RCO RCO2] = calc_prod_gas_com(r1,r2,r3,r4,r5);

end
```

d. Define reaction kinetics constraint equation

```
function [c,ceq] = kinetics_constants_EFB_PMFA_constraints(X)

A1=X(1);
E1=X(2);
A2=X(3);
E2=X(4);
A3=X(5);
E3=X(6);
A4=X(7);
E4=X(8);
A5=X(9);
E5=X(10);

global EH2a; %experimental value of H2 at 873K
global EH2b; %experimental value of H2 at 973K
global EH2c; %experimental value of H2 at 1073K


global ECOa; %experimental value of CO at 873K
global ECOb; %experimental value of CO at 973K
global ECOc; %experimental value of CO at 1073K


global ECO2a; %experimental value of CO2 at 873K
global ECO2b; %experimental value of CO2 at 973K
global ECO2c; %experimental value of CO2 at 1073K




n = 3;  % Number of intervals
T = linspace(873,1073,n);

for i=1:n

[RH2(i) RCO(i) CO2(i)] =
run_reaction_kinetics_model_kinetics_parameters(T(i),A1,E1,A2,E
2,A3,E3,A4,E4,A5,E5);


end

ceq=[];

c(1)=EH2a-RH2(1);
c(2)=EH2b-RH2(2);
c(3)=EH2c-RH2(3);

c(4)=ECOa-RCO(1);
c(5)=ECOb-RCO(2);
c(6)=ECOc-RCO(3);

c(7)=ECO2a-RCO2(1);
c(8)=ECO2b-RCO2(2);
```

```
c(9)=ECO2c-RCO2(3);

end
```

e. Define Temperature intervals

```
function [MTD]= run_kinetics_constants_EFB_PFMA(X)

A1=X(1);
E1=X(2);
A2=X(3);
E2=X(4);
A3=X(5);
E3=X(6);
A4=X(7);
E4=X(8);
A5=X(9);
E5=X(10);

global ERT;

n = 3;  % number of intervals
T = linspace(873,1073,n);

for i=1:n

[RH2(i) RCO(i) RCO2(i)] =
run_reaction_kinetics_model_kinetics_parameters(T(i),A1,E1,A2,E
2,A3,E3,A4,E4,A5,E5);

RT(i)=RH2(i)+RCO(i)+RCO2(i);

end

MTD=(RT(1)+RT(2)+RT(3))-ERT;

end
```

4.1.2 MATLAB Main File (M-File) for optimization calculation

```
% Script file for Parameters Modelling Fitting approach

global EFB; %EFB feedrate

global ERT; %total percentage of yields

global EH2a; %experimental value of H2 at 873K
global EH2b; %experimental value of H2 at 973K
global EH2c; %experimental value of H2 at 1073K


global ECOa; %experimental value of CO at 873K
global ECOb; %experimental value of CO at 973K
global ECOc; %experimental value of CO at 1073K


global ECO2a; %experimental value of CO2 at 873K
global ECO2b; %experimental value of CO2 at 973K
global ECO2c; %experimental value of CO2 at 1073K

EFB=1600;

EH2a=2*100/(2+2.1+4);
EH2b=2.1*100/(2+2.1+4);
EH2c=4*100/(2+2.1+4);

ECOa=6*100/(6+6.5+7);
ECOb=6.5*100/(6+6.5+7);
ECOc=7*100/(6+6.5+7);

ECO2a=6.1*100/(6.1+5.8+8);
ECO2b=5.8*100/(6.1+5.8+8);
ECO2c=8*100/(6.1+5.8+8);

ERT=300;

% define the initial guess independent variables for
optimization
% [k1,E1,k2,E2,k3,E3,k4,E4,k5,E5,k6,E6]
X0=[2.71 10.783 1.75 2.56 0.18 4.12 3.45 6.29 1.87 1.94 6.123
8.13];
% define the lower bounds for independent variables
LB=[];
% define the upper bounds for independent variables
UB=[];

% define the coefficients for the linear inequality constraints
A = [];
B = [];

% define the coefficients for the linear equality constraints
Aeq = [];
Beq = [];
```

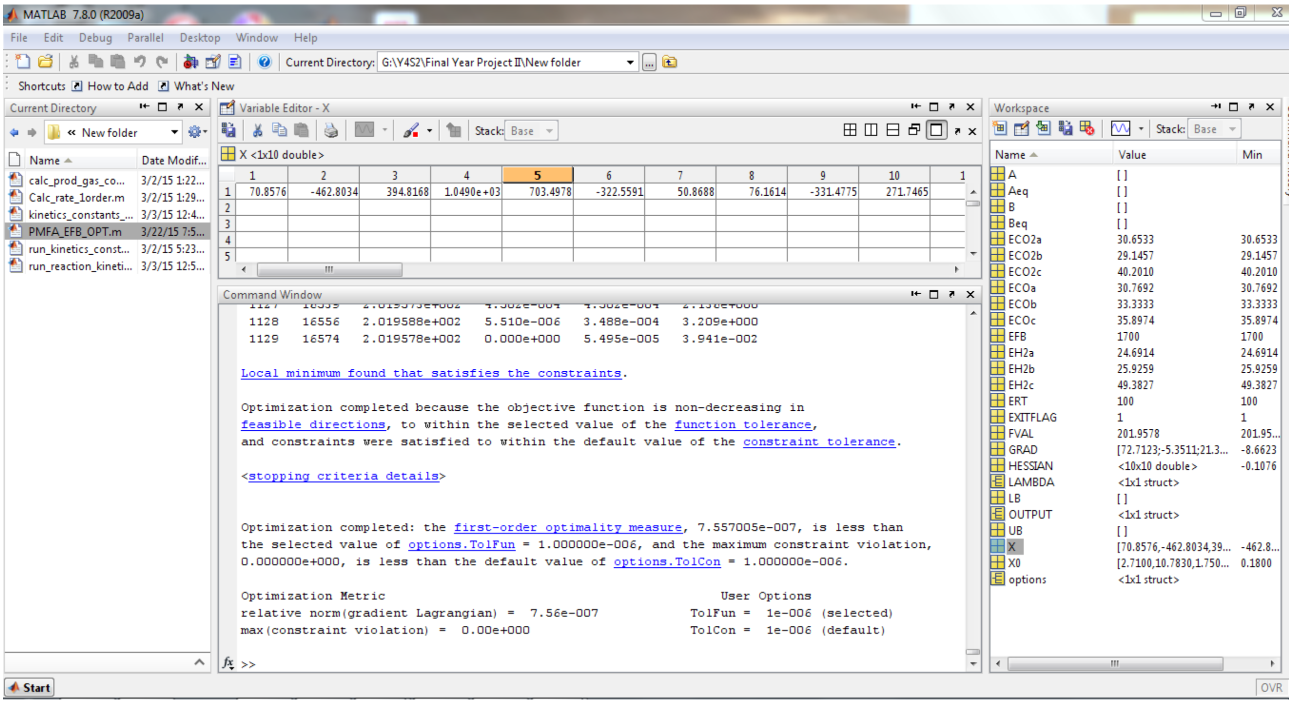
```
% The function NONLCON lists the nonlinear constraints

% define the options for the optimization solver

options = optimset('Algorithm','interior-point','Display',
'iter','MaxFunEvals',1e6,'MaxIter',1e6, ...
    'TolFun',1e-6,'TolConSQP',1e-6,'TolX',1e-
6,'FunValCheck','on');

% solving the optimization problem

[X,FVAL,EXITFLAG,OUTPUT,LAMBDA,GRAD,HESSIAN]=fmincon(@run_kinet
ics_constants_EFB_PFMA,X0,A,B,Aeq,Beq,LB,UB,@kinetics_constants
_EFB_PMFA_constraints,options);
```



Name	Date Modif...
calc_prod_gas_co...	3/2/15 1:22...
Calc_rate_1order.m	3/2/15 1:29...
kinetics_constants_...	3/3/15 12:4...
PMFA_EFB_OPT.m	3/22/15 7:5...
run_kinetics_const...	3/2/15 5:23...
run_reaction_kineti...	3/3/15 12:5...

	1	2	3	4	5	6	7	8	9	10	1
1	70.8576	-462.8034	394.8168	1.0490e+03	703.4978	-322.5591	50.8688	76.1614	-331.4775	271.7465	
2											
3											
4											
5											

```
 1128    16556    2.019588e+002    5.510e-006    3.488e-004    3.209e+000
 1129    16574    2.019578e+002    0.000e+000    5.495e-005    3.941e-002

Local minimum found that satisfies the constraints.

Optimization completed because the objective function is non-decreasing in
feasible directions, to within the selected value of the function tolerance,
and constraints were satisfied to within the default value of the constraint tolerance.

<stopping criteria details>


Optimization completed: the first-order optimality measure, 7.557005e-007, is less than
the selected value of options.TolFun = 1.000000e-006, and the maximum constraint violation,
0.000000e+000, is less than the default value of options.TolCon = 1.000000e-006.

Optimization Metric                                          User Options
relative norm(gradient Lagrangian) =  7.56e-007          TolFun =  1e-006 (selected)
max(constraint violation) =  0.00e+000                   TolCon =  1e-006 (default)

>>
```

Name	Value	Min
A	[ ]	
Aeq	[ ]	
B	[ ]	
Beq	[ ]	
ECO2a	30.6533	30.6533
ECO2b	29.1457	29.1457
ECO2c	40.2010	40.2010
ECOa	30.7692	30.7692
ECOb	33.3333	33.3333
ECOc	35.8974	35.8974
EFB	1700	1700
EH2a	24.6914	24.6914
EH2b	25.9259	25.9259
EH2c	49.3827	49.3827
ERT	100	100
EXITFLAG	1	1
FVAL	201.9578	201.95...
GRAD	[72.7123;-5.3511;21.3...	-8.6623
HESSIAN	<10x10 double>	-0.1076
LAMBDA	<1x1 struct>	
LB	[ ]	
OUTPUT	<1x1 struct>	
UB	[ ]	
X	[70.8576,-462.8034,39...	-462.8...
X0	[2.7100,10.7830,1.750...	0.1800
options	<1x1 struct>	

Figure 7: Screenshot of MATLAB

Figure 7 shows screenshot of MATLAB program after optimization is conducted by using coding that has been developed in section above.

4.2 OPTIMIZATION RESULTS

$$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO \tag{1}$$

$$C_6H_6 + 12H_2O \rightarrow 15H_2 + 6CO_2 \tag{2}$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{3}$$

$$C_7H_8 + 7H_2O \rightarrow 11H_2 + 7CO \tag{4}$$

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2 \tag{5}$$

Reaction	A	Ea
1	70.858	-462.803
2	394.817	1048.977
3	703.498	-322.559
4	50.869	76.161
5	-331.478	271.747

Table 1: Arrhenius Constant, A and Activation Energy, Ea obtained from MATLAB Optimization approach.

4.3 REACTION RATE CALCULATION

Based on the optimization calculation from MATLAB, rate of reaction at various temperatures can be calculated by using parameters obtained as shown in Table 1.

Temperature (K)	873	923	973	1023	1073	1123
1	120.398	116.990	114.014	111.394	109.070	106.995
2	118.729	126.714	134.335	141.603	148.533	155.141
3	1017.952	997.780	980.021	964.270	950.206	937.573
4	46.619	46.840	47.039	47.219	47.383	47.533
5	-242.810	-246.940	-250.704	-254.150	-257.315	-260.233

Table 2: Reaction rate constant calculation

4.3.1 Volumetric rate of products

From reaction rate constant obtained as shown in Table 2, volumetric rate for each product can be calculated by using kinetic model developed as shown in the equations below.

$$R_{H_2} = 9r_1 + 15r_2 + r_3 + 15r_4 + 18r_5 \quad (6)$$

$$R_{CO} = 6r_1 - r_3 + 7r_4 \quad (7)$$

$$R_{CO_2} = 6r_2 + r_3 + 7r_5 \quad (8)$$

Product	873	923	973	1023	1073	1123
H_2	24.691	21.728	25.926	35.580	49.383	66.325
CO	30.769	32.037	33.333	34.627	35.897	37.133
CO_2	30.653	29.489	31.103	34.842	40.201	46.790

Table 3: Volumetric Rate of various products at different temperatures

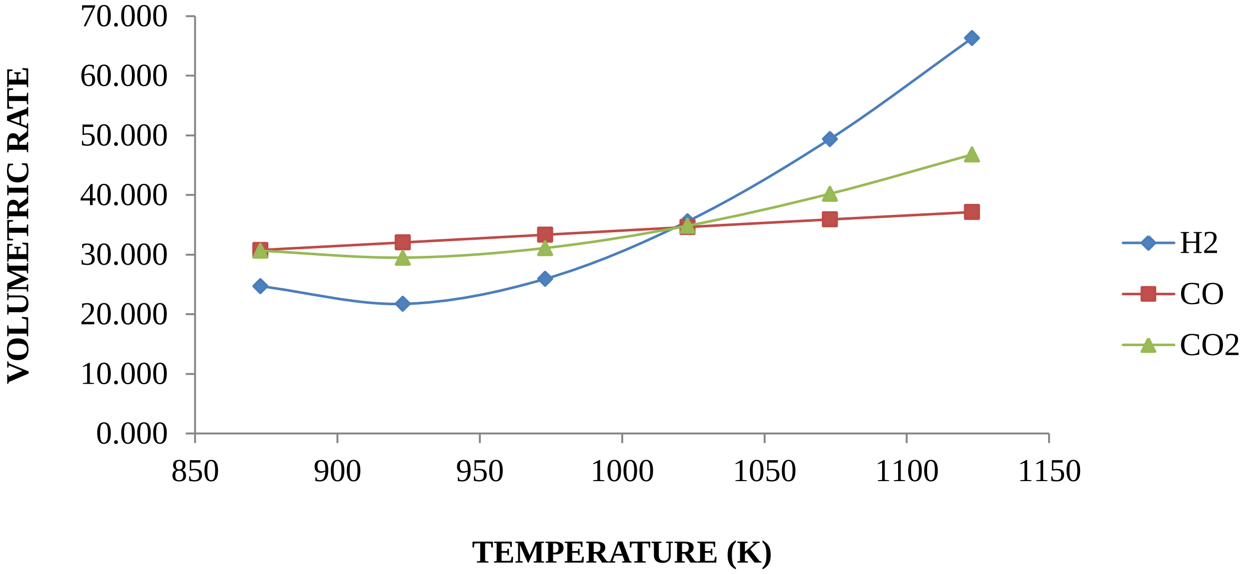


Figure 8: Graph of Volumetric Rate of products at different temperatures

From the graph as shown in Figure 8, production of Hydrogen increases exponentially as temperature increases. This may be due to the efficiency of thermal tar cracking where Hydrogen production can be increased as temperature increases.

$$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO \tag{1}$$

$$C_6H_6 + 12H_2O \rightarrow 15H_2 + 6CO_2 \tag{2}$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{3}$$

$$C_7H_8 + 7H_2O \rightarrow 11H_2 + 7CO \tag{4}$$

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2 \tag{5}$$

According to Simell et al. (1999) and Swierczynski et al. (2008), thermal cracking of benzene (equation 1 and 2) and toluene (equation 4 and 5) are endothermic reaction whereas Water-Gas Shift forward reaction (equation 3) is exothermic reaction. Therefore, increase in temperature favours the reaction to occur in production of Hydrogen, Carbon Monoxide as well as Carbon Dioxide. This also explains the increase of yield and ratio of Hydrogen production as shown in Figure 9 and Figure 10 respectively.

4.3.2 Yield of products

Products	873	923	973	1023	1073	1123
H2	0.287	0.261	0.287	0.339	0.394	0.441
CO	0.357	0.385	0.369	0.330	0.286	0.247
CO2	0.356	0.354	0.344	0.332	0.320	0.311

Table 4: Yield of products at different temperatures

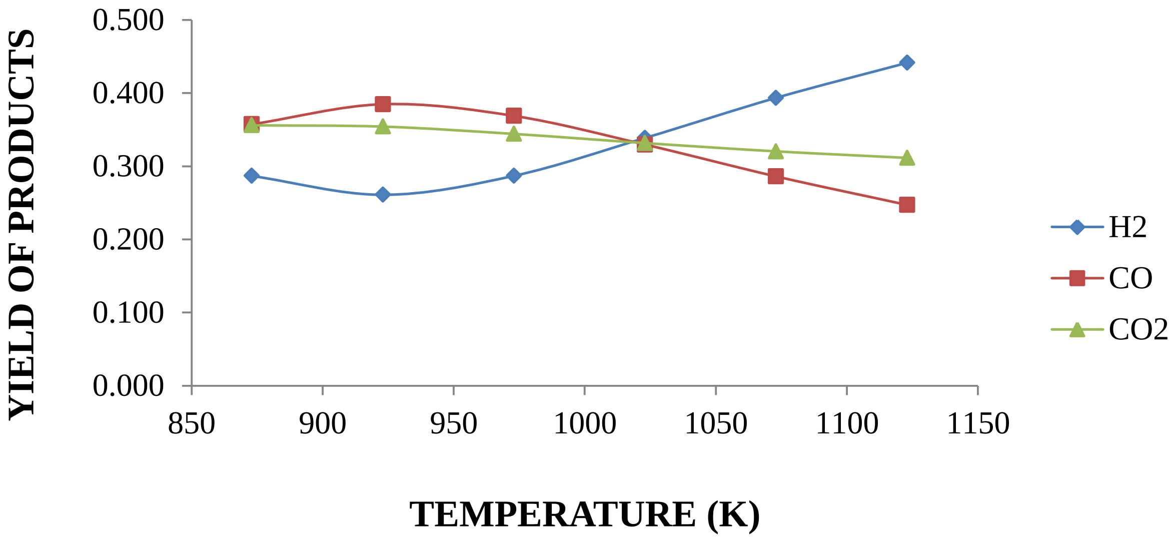


Figure 9: Graph of yield of products against Temperature

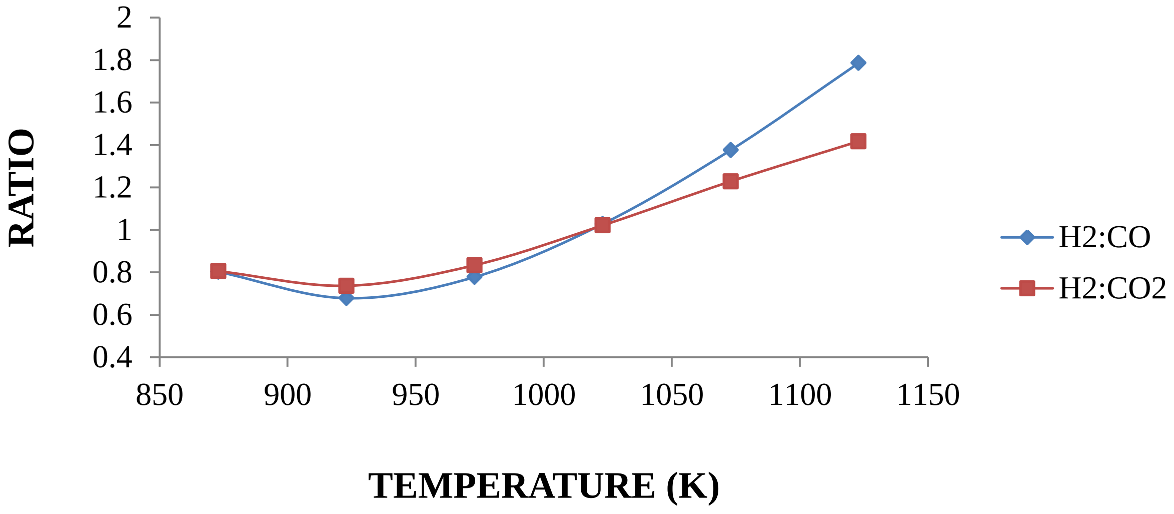


Figure 10: Graph of ratio of Hydrogen to CO and CO_2

4.3.2 Flammability Limit

Flammability limit is defined as a concentration range in which fire or explosion may occur due to the presence of flammable substance when an ignition source is present. Extra safety precaution should be taken if any concentration is between these flammability limits. Substances are difficult to be burnt or explode beyond upper flammability limit (UFL) due to deficient in oxygen or excess of air is presence whereas for lower flammability limit (LFL) is due to the lack of air or fuel for explosion to occur.

Lower and upper flammability limit can be calculated by using the formula

a. Lower Flammability Limit (LFL)

$$LFL_{mixture} = \frac{1}{\sum \frac{x_i}{LFL_i}}$$

b. Upper Flammability Limit (UFL)

$$UFL_{mixture} = \frac{1}{\sum \frac{x_i}{UFL_i}}$$

Flammability Limit	LFL	UFL
Hydrogen (H_2)	4	75
Carbon Monoxide (CO)	12	75

Table 5: Flammability Limit of H_2 and CO adapted from The Engineering Tool Box

Flammability Limit (Mixture)	873	923	973	1023	1073	1123
LFL	9.856	10.276	9.759	8.917	8.182	7.636
UFL	105.149	101.487	105.176	113.413	123.670	134.273

Table 6: Lower and Upper Flammability Limit of product mixture

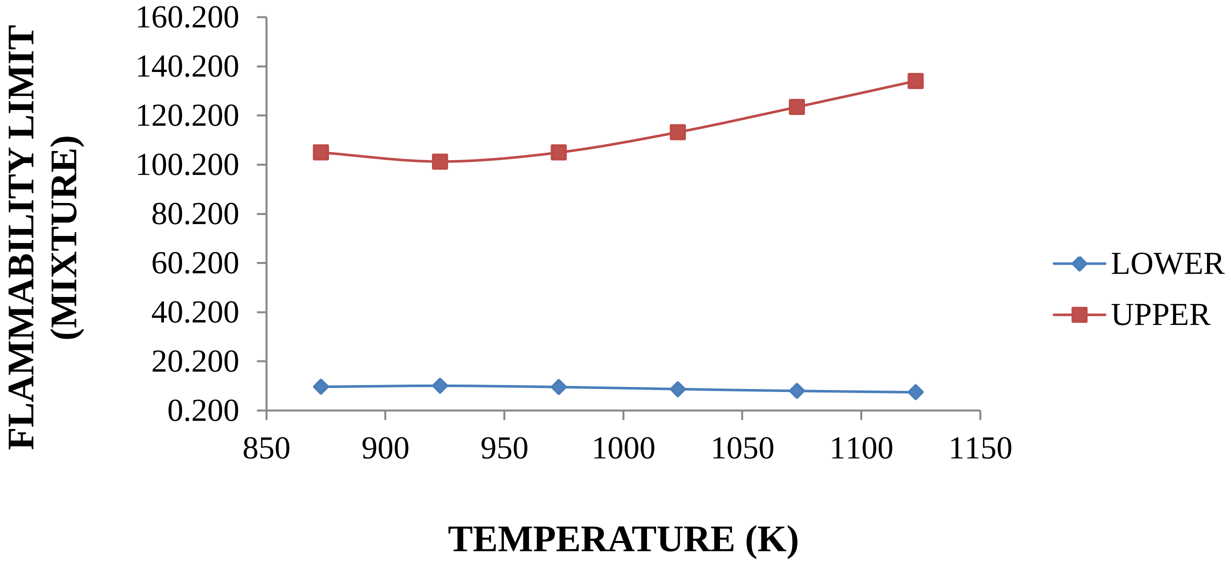


Figure 11: Graph of LFL and UFL Mixture against Temperature

Due to the increase in Hydrogen content as temperature increases, flammability limit range is increased as shown in Figure 11. Hydrogen gas is highly flammable and explosive may occur if there is any ignition source. Therefore the increase in Hydrogen content will result to a wider range of Flammability Limit. Carbon Dioxide gas however, is non-flammable gas and will not cause explosive. Thus presence of Carbon Dioxide will not affect the range of Flammability Limit.

4.4 MODEL VALIDITY

Yield	873	923	973	1023	1073	1123
MODEL	0.287	0.261	0.287	0.339	0.394	0.441
EXP	0.320	0.255	0.274	0.350	0.399	0.431
Error	0.115	0.022	0.045	0.035	0.014	0.023

Table 7: Comparison between model and experimental value

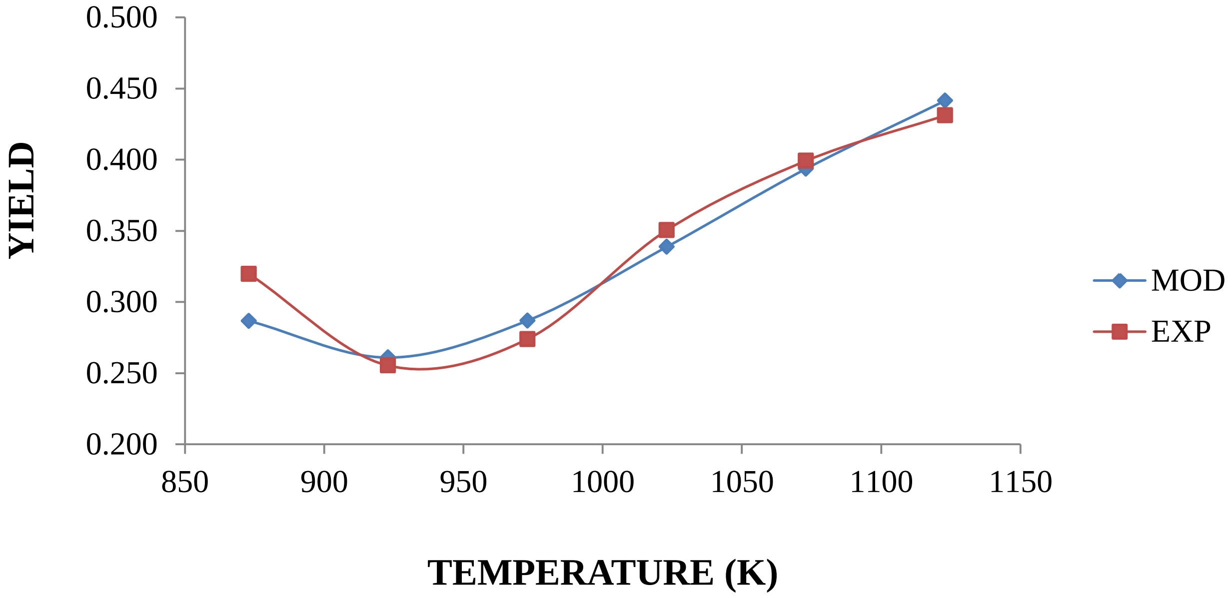


Figure 12: Graph of difference between model and experimental value for yield of Hydrogen production

Figure 12 shows the comparison of graphs between the yields of Hydrogen production obtained through modelling of this research project and experimental value obtained by Morf et al. It can be said that this model is valid as the difference between the model and experimental value does not differ much as shown in Figure 11.

5.0 CONCLUSION & RECOMMENDATION

5.1 CONCLUSION

Tar cracking in flue gas from biomass gasification is required for obtaining a feasible gasification process and more economical. The presence of tar in the gasifier will cause the decrease in efficiency of the biomass utility. Therefore, it is necessary to eliminate these decompositions of tar to maintain the utility efficiency as well as to maximize the production of useful products from biomass as well as tar cracking.

This research project is expected to help in tar cracking by developing the kinetic modelling of the reaction in tar cracking as well as to obtain the reaction constant of tar cracking in order to enhance energy production from biomass by maximizing the efficiency of producing Hydrogen as well as other useful products from biomass and tar cracking.

5.2 RECOMMENDATION

This research project is carried out by using simulation and optimization approach that can be justified theoretically and only based on one experimental journal. However this research project can be improvised by conducting laboratory or experiment in order to justify its feasibility of this research project.

REFERENCES

Brandt, P., & Henriksen, U. B. (2000). Decomposition of tar in gas from updraft gasifier by thermal cracking. In *Proceedings of 1. World Conference and Exhibition on Biomass for Energy and Industry*. Seville, Spain.

Bridgwater, A. V. (1995). The technical and economic feasibility of biomass gasification for power generation. *Fuel, 74*(5), 631-653. doi: http://dx.doi.org/10.1016/0016-2361(95)00001-L

Bui, T., Loof, R., & Bhattacharya, S. C. (1994). Multi-stage reactor for thermal gasification of wood. *Energy, 19*(4), 397-404.

Corella, J., Toledo, J. M., & Aznar, M.-P. (2002). Improving the Modeling of the Kinetics of the Catalytic Tar Elimination in Biomass Gasification. *Industrial & Engineering Chemistry Research, 41*(14), 3351-3356. doi: 10.1021/ie0110336

Devi, L., Ptasinski, K. J., & Janssen, F. J. J. G. (2003). A review of the primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy, 24*(2), 125-140. doi: http://dx.doi.org/10.1016/S0961-9534(02)00102-2

Evans, R. J., & Milne, T. A. (1987). Molecular characterization of the pyrolysis of biomass. *Energy & Fuels, 1*(2), 123-137. doi: 10.1021/ef00002a001

Han, J., & Kim, H. (2008). The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. *Renewable and Sustainable Energy Reviews, 12*(2), 397-416. doi: 10.1016/j.rser.2006.07.015

Houben, M. (2003). *Analysis of tar removal in a partial oxidation burner*: Technische Universiteit Eindhoven.

Li, C., & Suzuki, K. (2009). Tar property, analysis, reforming mechanism and model for biomass gasification—An overview. *Renewable and Sustainable Energy Reviews, 13*(3), 594-604. doi: 10.1016/j.rser.2008.01.009

Minkova V, M. S., Zanzi R, Bjornbom E, Budinova T, Stefanova M, Lakov L. (2000). Thermochemical treatment of biomass in a Iow of steam or in a mixture of steam and carbon dioxide. *Fuel Processing Technology, 62*, 8.

Morf, P., Hasler, P., & Nussbaumer, T. (2002). Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. *Fuel*, *81*(7), 843-853. doi: http://dx.doi.org/10.1016/S0016-2361(01)00216-2

Simell, P. A., Hirvensalo, E. K., Smolander, V. T., & Krause, A. O. I. (1999). Steam reforming of gasification gas tar over dolomite with benzene as a model compound. *Industrial & Engineering Chemistry Research, 38*(4), 1250-1257.

Swierczynski, D., Courson, C., & Kiennemann, A. (2008). Study of steam reforming of toluene used as model compound of tar produced by biomass gasification. *Chemical Engineering and Processing: Process Intensification*, *47*(3), 508-513. doi: http://dx.doi.org/10.1016/j.cep.2007.01.012

Tanksale, A., Beltramini, J. N., & Lu, G. M. (2010). A review of catalytic hydrogen production processes from biomass. *Renewable and Sustainable Energy Reviews*, *14*(1), 166-182. doi: 10.1016/j.rser.2009.08.010

World Development Indicators: Energy Prouction and use. (n.d.). Retrieved June 14, 2014, from The World Bank: http://wdi.worldbank.org/table/3.6