CHAPTER 4

METHODOLOGY

4.1 Biomass Analysis

Mimosa stalk samples were collected in Chiang Mai, Thailand. The collected stalks were cleaned and dried in a hot air oven in Figure 4.1. The dried samples were ground in a high speed rotary grinder in Figure 4.2. This was designed and constructed for crushing biomass from stalks to particles. The grinded biomass were sieving by vibratory screen sieve machine screen sieved in Figure 4.3. These feedstocks used for further analysis and experiments.

Figure 4.1 Hot air oven

Figure 4.2 The rotary grinder

Figure 4.3 Vibratory screen sieve machine

The samples for structural analysis were prepared in accordance with TAPPI T standards, in Table 4.1. The constituents of the biomass such as holocellulose, lignin and solvent extractive components were determined following TAPPI standard methods. The solubility of extractives in ethanol and benzene mixture, as well as, amount of soluble substances in sodium hydroxide and water were established.

The analysis methods of biomass as fuel are given in Table 4.2. The proximate and ultimate analyses of the samples were followed ASTM standard methods. A CHN elemental analyzer was used for determined the elements of biomass such as carbon, hydrogen and nitrogen and the oxygen content were calculated by difference.

A Parr bomb calorimeter was used for carry out the gross heating value of the samples following with ASTM 5865 standard.

Table 4.1 Structural analysis standard method

Property	Method
Holocellulose	Wise method
Lignin	TAPPI T 222
Extractives, soluble in ethanol and benzene	TAPPI T 204
Solubility in hot water	TAPPI T 207
Solubility in cold water	TAPPI T 207
Solubility in 1% NaOH solution	TAPPI T 212
Solubility in ethanol and benzene	TAPPI T 204

Table 4.2 Biomass fuel analysis methods

Property	Analytical Method	Property	Analytical Method
Proximate analysis (% w/w)		Ultimate analysis (% w/w)	
Moisture	ASTM D 3173	Carbon	ASTM D 3174
Volatile	ASTM D 3175	Hydrogen	ASTM D 3174
Fixed carbon	ASTM D 3172	Nitrogen	ASTM D 3174
Ash	ASTM D 3177	Oxygen	ASTM D 3174
H/C molar ratio	calculation	Higher heating value (MJ/kg)	ASTM 5865
O/C molar ratio	calculation		
Empirical formula	calculation		

4.2 Thermogravimetric Analysis

Thermal decomposition of the biomass was analyzed using a TGA/SDTA Mettler Toledo 851e. Thermogravimetric Analyzer shown in Figure 4.4, (sensitive microbalance, 0.1 µg resolution, 1600 ^{o}C maximum temperature at atmospheric pressure). The system is logged to a personal computer for data handling and analysis. Prior to TGA, temperature, weight, and sampling platform calibrations were carried out.

Figure 4.4 TGA/SDTA Mettler Toledo 851e Thermogravimetric Analyzer

Each sample was placed in the platinum crucible (70 ml) securely and in such a way that it was confined within the pan sides and not in contact with the sides of the oven. All handling of samples were done using brass tweezers to avoid contamination. Nonisothermal experiment runs were carried out at 10, 30, and 50 ^{o}C/min under atmospheric pressure, with an initial weight sample of 5 mg and a purge gas flow of 50cm^{3}/min. The purge gases used were high purity nitrogen, air or oxygen as medium with a flow rate of 50cm^3/min. The sample was heated from room temperature to programed temperature. The continuous records of weight loss and temperatures were record during heating. At least three runs were tested for each condition.

4.3 Fixed Bed Gasification

4.3.1 Rig Setup

The laboratory rig set up used in this study is a fixed bed reactor, schematically shown in Figure 4.5. The cylindrical reactor has an inside diameter of 40 mm and 0.5 m high. It has two sections such as cooling section (10) and heating section (8). Cooling section was feeding by water at room temperature. The heating zone is heated by a 5 kW heating coil and surrounded by ceramic fiber insulating. The inlet of reactor, on the upper cover of the reactor, is connected with gasifier agent such as air which feeding from compressed tank (1). The air was measured by flow meter (3). While the outlet is connected to a series of iso-propanol tubes for cooling and traps the tarry components (13). The gaseous products were measured by gas flow meter (14) and collected at the exit of the dry filter in a 0.40 dm^3 gas sampling bag (15) (FlexFoil from SKC with used for contain hydrogen, methane, carbon monoxide, carbon dioxide).

Reaction temperature is measured by a thermocouple (5) inserted thru its cover and can be automatically controlled by a temperature controller (7). Biomass temperature is measured by a thermocouple (6) and display by a temperature controller (7).

4.3.2 Experimental Procedure

The dry samples (0%, of moisture) with, in the size range of 3 – 6 mm, were used. A fixed grate was preweighted and loaded samples for 10 g. Air zero (UHP grade), from a compressed tank, is supplied for serving as a purge gas and protective gas to avoid coking, which occurred on the surface of the reactor before and after

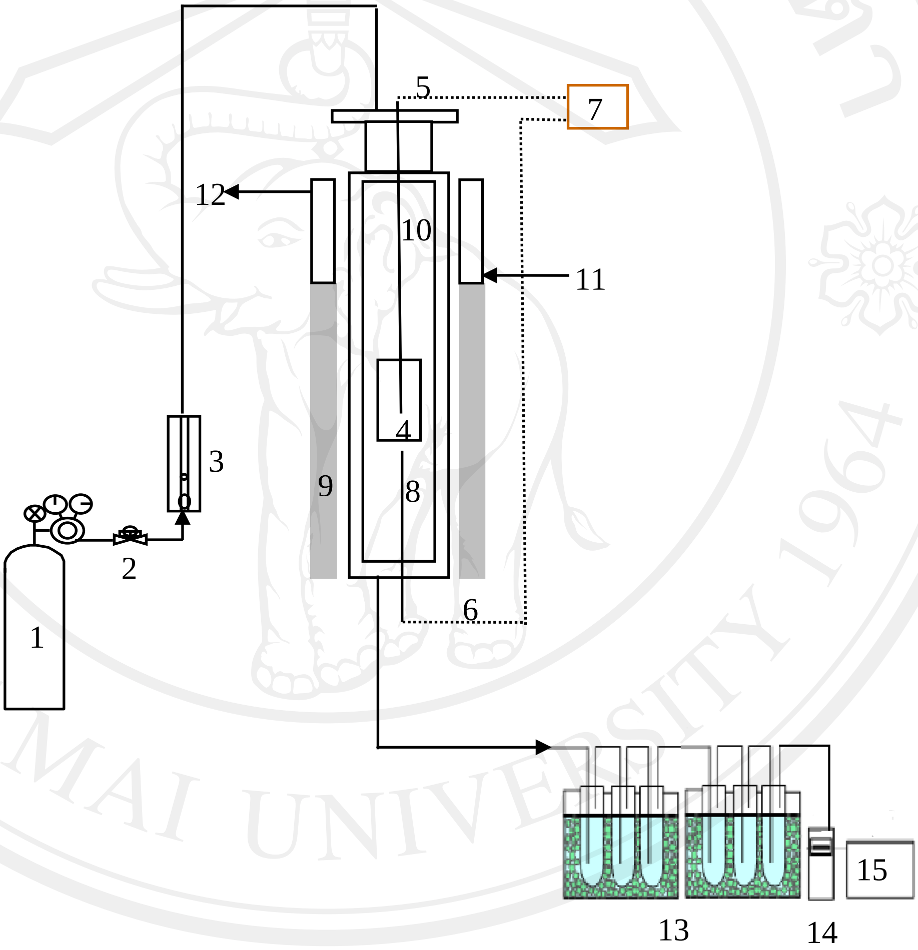


Figure 4.5 Schematic diagram of a fixed bed reactor: (1) air compressed tank, (2) valve, (3) flow meter, (4) fixed grate, (5) sample thermocouple, (6) reactor thermocouple, (7) temperature controller, (8) heating section, (9) electrical heater and insulator, (10) cooling section, (11) cooling water inlet, (12) cooling water outlet, (13) tar remover section, (14) gas flow meter and (15) gas bag.

operation. The air flow rate with 100 cc/min (ER 0.25) was measured with a calibrated flow meter and compared with a gas volume meter.

A samples temperature and gasification temperature are measured by a thermocouple inserted thru its upper cover and its exit, respectively. The temperatures are measured and automatically controlled by means of temperature controllers. The reactor temperature was obtained from thermocouple readings inside the reactor at heating section and represented as gasification temperature.

Two heating rates with 10 and 100-150 ^{o}C/min were conducted in this gasification system. With heating rate of 10^{o}C/min, biomass and reactor were heated together from the room temperature.

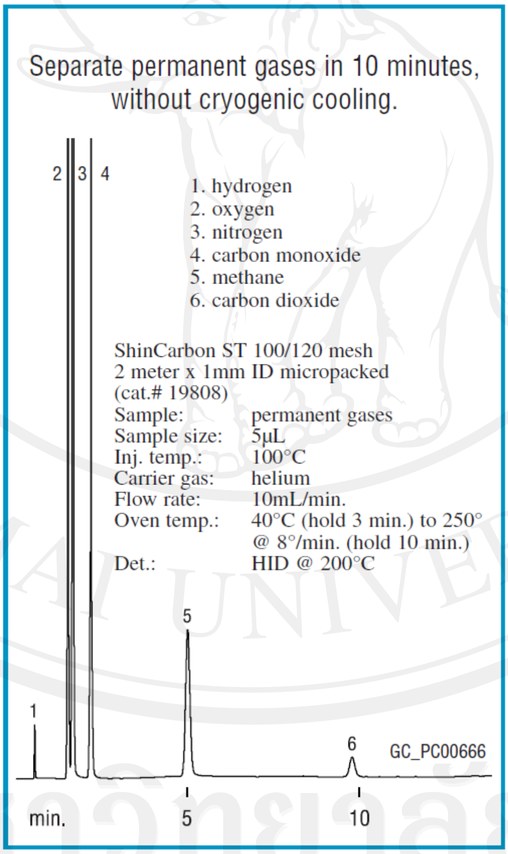
With higher heating was conducted following the process. Prior to test, the heating section of the reactor was heated externally by an electrical heater until reaching the setting temperature and still waiting for about 30 min before started an experiment.

A fixed grate, contained samples inside, was introduced into the cooling section of the reactor, after that the reactor was closed. The gasification agent such as the air was supplied to the reactor. After that, the fixed grate was moved from a cooling zone to a heating zone or oxidation zone inside the reactor. A gasification process can be occurred, and gaseous products from the biomass went out at the exit of reactor. A gasification time was processed for 110 min. After 110 min, a fixed grate was moved to cooling section and then it was purged with N_2 as gasification agent. When the samples temperatures decrease until reached the room temperature, it was removed from the reactor. At the end of every experiment, the solid and liquid residues were weighed to determine mass balance. The gas yields were computed directly, based on its measured volume.

The gaseous products were collected at the exit of the dry filter in a gas sampling bag. They were immediately sent to analysis for composition and yields such as CO, CO_2, H_2, CH_4, and N_2 by a Shimadzu Gas Chromatography model GC-8A shown in Figure 4.6. Results are processed and printed via C-R8A chromatopac data processor. GC is connected with TCD detector which Micropacked column is named Shin carbon ST 80/100 mesh. The high purity standard gases were used to calibrate the instrument in Figure 4.7. Scotty (Air liquid) 14 contains carbon monoxide, carbon dioxide, nitrogen, and oxygen, (5% each) and methane and hydrogen (4% each) in helium. Gas pressure is 240 psig or 17 bar and volume of 14 liters. Its example chromatogram is shown in Figure 4.8. The operation conditions are column oven temperature of 30 ^{o}C and detector temperature of 70 ^{o}C.

Figure 4.6 Shimadzu Gas Chromatography model GC-8A. and C-R8A Chromatopac data processes

Figure 4.7 Air, Pure Gases and mixtures standard (Restek, 2012)



Separate permanent gases in 10 minutes, without cryogenic cooling.

1. hydrogen
2. oxygen
3. nitrogen
4. carbon monoxide
5. methane
6. carbon dioxide

ShinCarbon ST 100/120 mesh
2 meter x 1mm ID micropacked
(cat.# 19808)

Sample:	permanent gases
Sample size:	5µL
Inj. temp.:	100°C
Carrier gas:	helium
Flow rate:	10mL/min.
Oven temp.:	40°C (hold 3 min.) to 250° @ 8°/min. (hold 10 min.)
Det.:	HID @ 200°C

Figure 4.8 Shin Carbon ST Micropacked GC columns (Restek, 2012)

4.4 Fluidized Bed Gasification

4.4.1 Rig Setup

A schematic of the fluidized bed gasification system shows in Figure 4.9. Its main components include: a fluidized bed reactor (7, 9, 10, and 11), a biomass feeder (8), and gasifying medium feeder. A series of gasification medium supply at an inlet of the reactor compose of air compressor (1), a control valve (2), flow meter (3), an air preheater (4). The exit are cyclone (12), gas traps and cleaning (13), silica gel (14), pump (15), gas volume meter (16) and gas sampling bag (17). The heat supply unit composes of gas tank (5) and gas burners (6).

The fluidized bed reactor height was 2 m with inside diameter of 50 mm. It was made from stainless steel cylinder and was externally covered with insulator. The thermocouples were installed with along the length of reactor in order to determine the temperature distribution inside the reactor while fluidizing. Below the reactor, an air plenum and an air distributor are installed for stable pressure and air distribution. The samples were fed into the reactor through a screw feeder at rates of 10-20 g/min.

The gasification medium was air with flow rate of 20 lpm. It was preheated to 300-400^{o}C by air preheater and at the plenum before entered into the reactor. The bed temperature is controlled for gasification temperature measure by thermocouple.

The produced gas exits the reactor via a cyclone, into gas cleaning system. The exit gas was analyzed by the (model GC-8A of Shimudzu) as same as analysis of gas products from the experiment of fixed bed gasification.

4.4.2 Experimental Procedure

Each run was started by filling the bed with silica sand 10g, or silica sand mixed with dolomite up to the desired weight with 10:10 g. The propane shut-off valve was opened, and then the burner was turned on, after that the air valued was opened to supply enrich oxygen to the burners. In the start-up period, the bed was preheated to the setting temperature before feeding the biomass.

It takes about 60 min to preheat silica sand to reach the bed setting temperature. The air was supplied from air compressor through the preheater, air distributor, and into the reactor. Until the bed temperature remained constant, the screw feeder fed biomass from the hopper into the reactor at the upper of the bed or bottom of the reactor. Biomass was fed at 10 g/min, and air was supplied at 15 lpm continuously carried out at constant flow rate

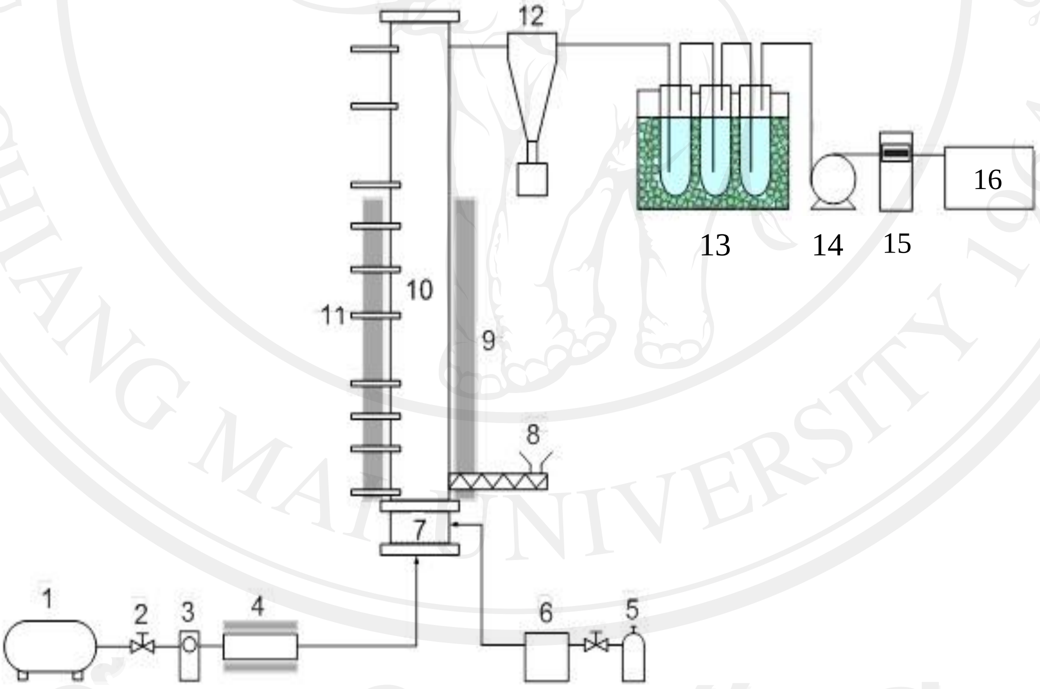


Figure 4.9 Schematic diagram of a fluidized bed reactor:(1) air pump, (2) valve, (3) flow meter, (4) preheater, (5) LPG tank, (6) burner, (7) distributor, (8) biomass feed hopper, (9) insulator, (10) fluidized bed reactor, (11) thermocouple, (12) cyclone, (13) tar remover section, (14) pump, (15) gas flow meter, and (16) gas bag.

After the bed temperature was steady, and then the gasification processes occurred. The produced gases were generated and exit the reactor. The product gas passed through the tar trap system for cleaning. The clean gases were collected by gas bags and then analyzed by gas chromatography, for H_2, O_2, N_2, CH_4, CO and CO_2. The gas chromatograph was calibrated by using standard gases. Each condition was repeated at least three times. The char was collected in the cyclone, and in the reactor.

4.5 Data Collection and Analysis

4.5.1 Mass Balance

In fixed bed and fluidized bed gasification, the mass of biomass ($m_{biomass}$) was preweighted before every experiements. The products are gas, solid and liquid. The gas volume (V_{gas}) was measured by the gas meter. The mass of solid (m_{solid}, char and ash) was weight after finish the process. The mass of liquid (m_{liquid}) was weight the tar remover section that is a series of 6 glass tubes. The mass of gas is calculated from the following equation.

$$P_{gas}V_{gas} = m_{gas}RT \tag{4.1}$$

P_{gas} = Pressure of gas products (m^3/kg)

V_{gas} = Volume of gas products (m^3)

m_{gas} = mass of gas products (kg)

R = Universal gas constant (8.31446 J/(mol K))

T = Temperature (K)

The mass balance for gasification process as follow equation

$$m_{biomass} = m_{gas} + m_{liquid} + m_{solid} \tag{4.2}$$

4.5.2 Equivalent Ratio

The equivalent ratio (ER) is the variable that compares the various of biomass air gasification.

$$ER = \frac{Gasification\ ratio(GR)}{stoichiometric\ ratio(SR)} = \frac{(A/F)_{actual}}{(A/F)_{stoichiometry}} \tag{4.3}$$

4.5.3 Stoichiometric Ratio

The stoichiometric ratio can be calculated from carbon, hydrogen and oxygen content in biomass as follow equation (Zhu and Venderbosch, 2005).

$$SR = \left(\frac{C\%}{12} + \frac{H\%}{4} - \frac{O\%}{32}\right)\left(1 + \frac{79}{21}\right)\left(1 - \frac{Ash\%}{100}\right)\frac{28.84}{100} \tag{4.4}$$

$C\%$ = Carbon content in the ultimate analysis (%)

$H\%$ = Hydrogen content in the ultimate analysis (%)

$O\%$ = Oxygen content in the ultimate analysis (%)

$Ash\%$ = Ash content in the proximate analysis (%)

4.5.4 Product Gas Analysis and Conversion

Gas mixture standard was analyzed by GC and collected the chromatogram area for the mixture gases. The area was the average value from five experiments.

$$conversion\ ratio = \frac{Gas\ standard\ (\%mol)}{GC\ area} \tag{4.5}$$

Table 4.3 Gas standard composition and conversion

	Gas Standard(%mol)	GC area	Conversion ratio
H_2	4	181	0.022075
O_2	5	10528	0.000475
N_2	4.99	15829	0.000315
CO	5.03	10695	0.00047
CO_2	4	7003	0.000571
CH_4	5	7681	0.000651
He	71.98	-	-
total	100	-	-

4.5.5 Carbon Conversion Efficiency

Carbon elements in any materials were measured by CHNO analysis (Lv et al., 2004).

$$\eta_c = \frac{V_{gas} \times \frac{[CH_4\% + CO\% + CO_2\%]}{100} \times 12/22.4 \times 100\%}{W\left(1 - \frac{ash\%}{100}\right) \times \frac{C\%}{100}} \tag{4.6}$$

η_c Carbon conversion efficiency (%)

V_{gas} = Volume of gas products (litre)

CH_4,CO, CO_2 = Gas concentrations (vol%)

W = Dry biomass feeding (g)

4.5.6 Gas Heating Value

The low heating value of gas product is calorific value of gas from dry biomass (Lv et al., 2004)

$$LHV = \frac{(30 \times CO\% + 25.7 \times H_2\% + 85.4 \times CH_4\%)}{100} \times 4.2\ (kJ/Nm^3) \tag{4.7}$$

4.5.7 Gasification Efficiency

The efficiency of gasification process in any reactor can be calculated from following equation

$$\eta_g = \frac{V_{gas} \times gas\ heating\ value(kJ/Nm^3)}{W \times biomass\ heating\ value(kJ/kg)} \times 100\% \tag{4.8}$$

η_g = Gasification efficiency (%)

V_{gas} = Volume of gas products (m^3)

W = Dry biomass feeding (kg)

4.6 Gasification Modeling

In this research, the stoichiometric approach was used to determine the syngas composition. The model was run with an elemental composition of biomass feedstocks. The feedstocks used in the model include mimosa stalk and bamboo. Syngas composition was determined by solving nonlinear equations using Newton-Raphson method as shown in Figure 4.10.

In this research, the model is used to determine syngas compositions from fixed bed and fluidized bed with various types of biomass and gasifying medium.

Methodology for Equilibrium Approach

1. Write the overall reaction of biomass with used gasification medium.

2. Taking atom balances based on elements evolved in the reaction like C, O_2, H_2, etc.

3. Write the equilibrium relations for gasification reactions like steam gasification, bouduard, and methanation reactions.

4. Solve the obtained system of algebraic equations simultaneously in order to determine the product yields.

5. Calculation the energy balance and check the errors.

6. Calculation the root mean square error between model and experiment data

$$RMSE = \sqrt{\frac{\sum_i (y_i - x_i)^2}{N}} \tag{4.9}$$

y_i = value from experiments

x_i = value from model prediction

N = number of data

subscript i = mol faction value of experiments

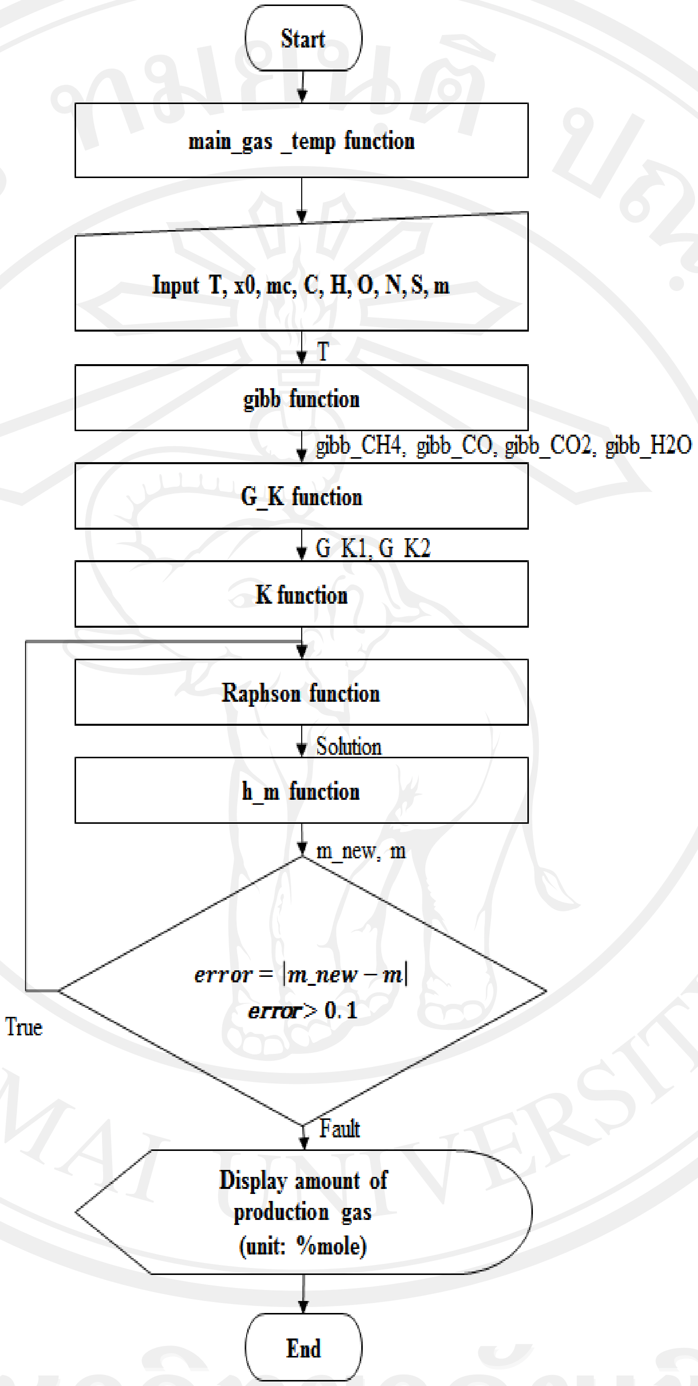


Figure 4.10 Gasification modeling diagram