CHAPTER 3

RESEARCH METHODOLOGY

3.1 Microwave Plasma System

The microwave plasma system in this work is the waveguide discharge type. It was assembled from a microwave plasma reactor, a gas injection system and a gas treatment system. The main objective of the plasma system is to generate the plasma in the reaction zone of the reactor. The plasma was used for plasmochemical conversion of solid waste. The design of plasma reactor and gas treatment system was detailed as follow.

3.1.1 Reactor

In this thesis, the microwave plasma reactor was modified from a commercial microwave oven as shown in Figure 3.1. The oven cavity with width of 295 mm, height of 180 mm, and deep of 255 mm was modified for the installation of the reaction tube as shown in Figure 3.2. A reaction tube made of quartz with internal and external diameters of 27 and 30 mm, and length of 250 mm was installed vertically at the central cavity of the oven as Figure 3.3. It was cooled outside the cavity on the top and bottom of the oven using a water cooling system as shown in Figure 3.4. Microwave radiation with magnetron power input of 800 W and frequency of 2.45 GHz was passed through the waveguide which installed at the right side wall of the

oven cavity. The manufactured waveguide consisted of a metal bump which acted like a circulator that protect a magnetron from the reflected power.

3.1.2 Gas Injection System

To generate the plasma, carrier gas or plasma gas was injected to the reaction zone. Argon was used as the plasma gas in this thesis. Its flow rate and pressure were controlled using a standard flow meter and a pressure regulator, as shown in Figures 3.5 and 3.6, respectively. The argon flow rate was in the range of 0.50 to 1.25 lpm. The carrier gas was fed into the bottom of the reaction tube at atmospheric pressure. It was passed through the reaction zone and ionized into plasma. At the reaction zone, the feedstock was converted into plasmochemical conversion products, such as synthesis gas, solid and liquid products. Gaseous and liquid products were carried to the top of the reaction tube with argon flow. The main objective of the plasma system in this thesis is to generate the fuel gas. Therefore, liquid products, such as tar and moisture were removed using gas treatment.

Figure 3.1 A schematic view of the microwave plasma system.
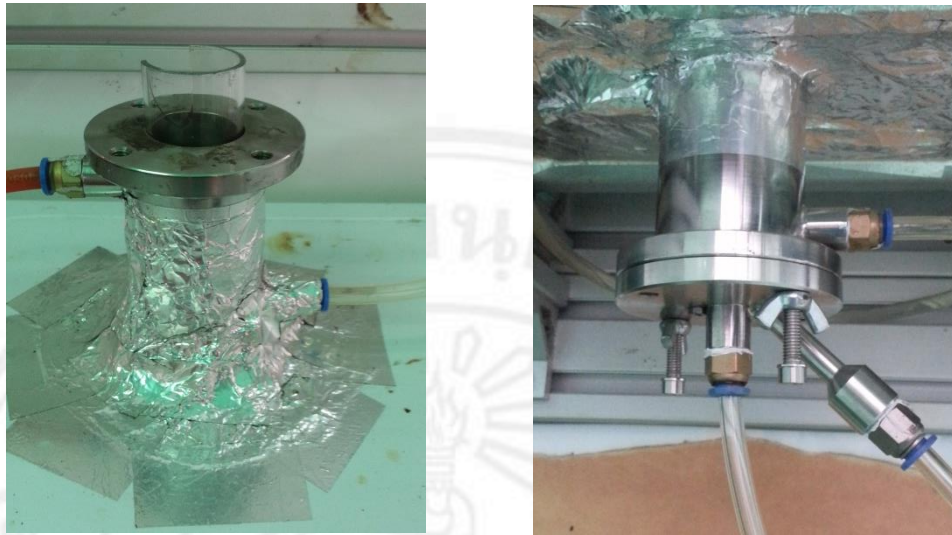
(a)   (b)

Figure 3.2 A modified microwave oven cavity,

(a) modified top wall and (b) modified bottom wall

Figure 3.3 The installation of reaction tube in the modified oven cavity.

(a)   (b)

Figure 3.4 The water cooling system of reaction tube,

(a) top and (b) bottom of the oven

Figure 3.5 A standard gas flow meter

Figure 3.6 A pressure regulator for argon

3.1.3 Gas Treatment System

In this thesis, the main products were gas, solid, and liquid. Solid products, such as fly ash and dust were removed with filter equipments as shown in Figure 3.7. Gaseous product consisted of fuel gases, volatiles, tar vapor, and moisture. Tar and moisture would damage the gas detecting column of the gas chromatography (GC). They had to be removed from a sample gas before injected to GC using gas treatment equipments. In order to remove tars from the sample gas, a tar removal equipment was used. The tar trap was assembled from six glass tubes. Each tube contained the isopropanol of 250 cm^3. A stack of glass tubes was placed in the ice bath as shown in Figure 3.8. The tar vapor was condensed and absorbed by isopropanol at low temperature. Moisture content in the product gas was captured by the silica gels.

Figure 3.7 Filter equipments

Figure 3.8 A stack of glass tubes, each contained the isopropanol of 250 cm^3

which used as tar trap in this thesis

3.2 Feedstock

3.2.1 Feedstock Preparation

In this thesis, the main combustible fractions of MSW (paper, biomass, and plastic) were used, as single component and in the form of RDF. Raw materials were obtained locally from the same source; (i) office paper was chosen as a representative of the waste paper fraction, (ii) bamboo was chosen as a representative of the biomass fraction and (iii) polyethylene (PE) taken from transparent plastic bottles was chosen to represent the plastic fraction. The data for PE was taken from a published report (Mastellone et al., 2002).

As for the plasmochemical conversion experiments, bamboo and PE were prepared into small pieces with diameter about 2 mm and length about 30 mm. A number of bamboo and PE pieces were banded by wire as shown in Figures 3.9 and 3.10. Each sample mass was about 3 ± 0.1 g. Paper was mashed, compacted into a cylindrical mold with diameter of 20 mm and length of 40 mm as shown in Figure 3.11, and dried in a hot air oven at 90°C for 48 h. After drying process, each sample mass was about 5 ± 0.1 g. Simulated RDF consisted of 30% paper, 20% PE, and 50% bamboo. All of raw materials were ground in a high speed rotary grinder. The grinded sample were mixed, and compacted into a cylindrical mold with 20 mm in diameter and 40 mm long as shown in Figure 3.12, and dried in a hot air oven at 90°C for 48 h. After drying process, each sample mass was about 8 ± 0.1 g.
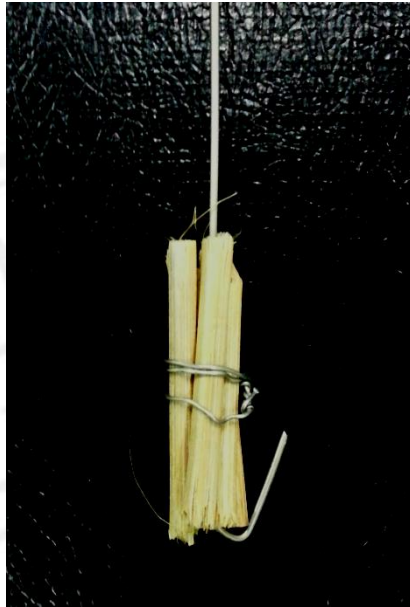
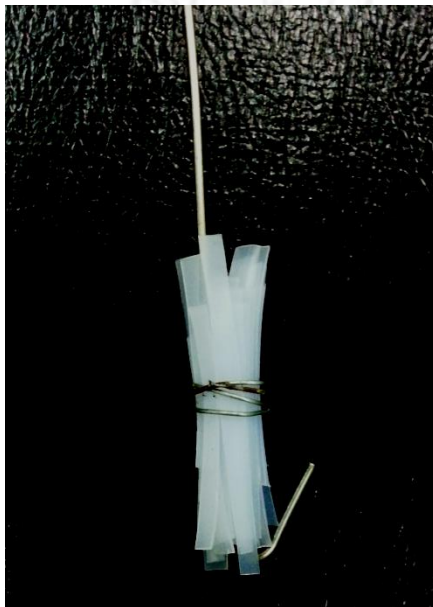Figure 3.9 Sample bamboo which used as a representative of the biomass feedstock

Figure 3.10 Sample PE which used as a representative of the plastic feedstock

Figure 3.11 Compressed paper which used as a representative of the paper feedstock

Figure 3.12 Sample RDF which used as feedstock in this thesis

3.2.2 Composition Analysis

In this thesis, thermogravimetric analysis (TGA) was used to determine moisture content, volatile matter, fixed carbon, and ash in the feedstock. The raw material was heated to observe the mass change as a function of temperature and time. Proximate analyses of RDF, its components, and chars were carried out by thermogravimetric method using a Perkin Elmer, model TGA7 instrument. The raw material was heated from 50 to 135 ℃ with heating rate of 10 ℃/min under nitrogen environment and held the temperature of 135 ℃ for 5 min. It was then heated from 135 to 900 ℃ with heating rate of 100 ℃/min under nitrogen environment. At reaction temperature of 900 ℃ oxygen was fed and held for 20 min.

A CHNS-O elemental analyzer was used to determine the elements of feedstock such as carbon, hydrogen, and nitrogen, whereas oxygen content were calculated by difference. Ultimate analyses were carried out by dynamic flash combustion method using a ThermoQuest, model Flash EA 1112 CHNS-O analyzer. The proximate and ultimate analyses of the samples were followed ASTM standard methods. The analysis methods of raw materials as fuel are given in Table 3.1.

Table 3.1 Feedstock Analysis Methods

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

3.3 Experimental Setup and Procedure

The experimental setup was shown schematically in Figure 3.13. It consists of a plasma reactor and a gas cooling and cleaning unit. A commercial microwave oven was modified into a plasma generator system. A quartz reactor tube was installed

vertically at the central cavity of the oven. The unit was cooled using a water cooling system. A 2.45 GHz microwave radiation with constant magnetron input power of 800 W was supplied continuously to the microwave cavity. A stainless steel wire was used as a hanger for feedstock tested. The plasma generated inside the reactor tube was initiated from electromagnetic stress concentration at the wire tip, inducing the carrier gas into ionized phase.

Prior to each test run, the reactor system was vacuumed to ensure an absence of air. Argon was used as the carrier gas. It is a relatively cheap, stable, long-lived ion stabilizer, and can enlarge electron density (Karches et al., 2001). The carrier gas was fed at the bottom of the reactor to purge oxygen in all systems, including the reactor tube, pipeline, and the gas treatment unit. The argon flow rate was varied between 0.50 to 1.25 lpm. It was fed tangentially as a swirling flow to confine the plasma flame and increase the residence time within the reactor. The feedstock was placed into the center of the quartz tube, direct to the aperture of the wave guide in the oven cavity. Once the power was switched on, the discharge took place inside the reaction tube, engulfed the feedstock and converted it into pyrolysis products. The product gas flowed out at the top of the reactor tube and though the gas treatment unit. After treated, product gas was sampled using a Restek multi-layer foil gas sampling bag for subsequent gas chromatographic analysis. Tar in the gas product was collected in a wet type tar trap using a series of isopropanal tubes placed in an ice bath. Moisture was removed in a silica gel chamber. After 3 min of reaction, the solid residue was carefully collected, weighed and sent for analyses.
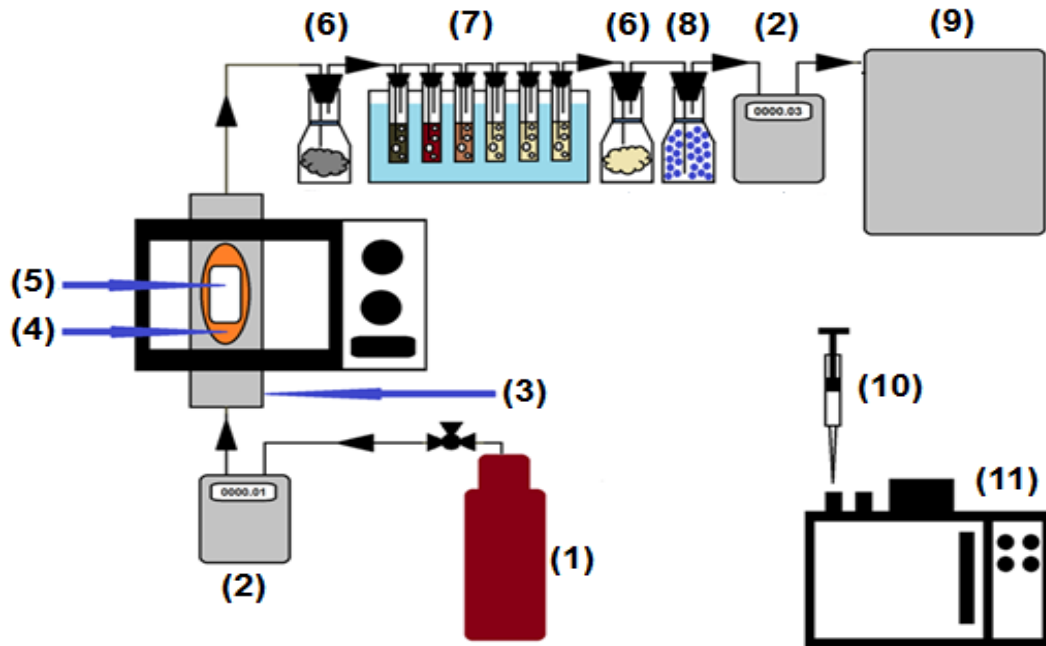
Figure 3.13 Experimental setup of the microwave plasma reactor

for pyrolysis of RDF, (1) argon tank, (2) flow meter, (3) reaction tube,

(4) plasma flame, (5) feedstock,(6) filter, (7) tar trap, (8) dryer, (9) gas bag,

(10) sample product gas, and (11) gas chromatography

3.4 Data Processing

3.4.1 Plasma Characteristics

Plasma characteristics including temperature, discharge length, and volume as well as power density were evaluated. The plasma temperature was measured indirectly by a thermocouple placed at a distance of 70 mm upstream of the discharge zone inside the quartz tube. The discharge length was measured from the discharge images captured by a digital camera. The discharge volume was calculated from its

length multiplied by a cross section area of the reaction tube. The power density was defined as a ratio between the input microwave power and the discharge volume.

3.4.2 Product Gas Analysis and Conversion

The product gas was collected at the exit of the dry filter in a gas sampling bag and analyzed for its composition using a Shimadzu model GC-8A gas chromatography, fitted with a Micropacked column model ShinCarbon ST 80/100 mesh and a TCD, shown in Figure 3.14 (a). The analyzer was able to measure the molar fractions of H_2, O_2, N_2, CH_4, CO and CO_2, respectively. The operational column temperature of 40°C and detector temperature of 70°C were used. Results were processed via a C-R8A chromatopac data processor, shown in Figure 3.14 (b). The Restek pure gases and mixtures standard model Scotty 14 contains carbon monoxide, carbon dioxide, nitrogen, and oxygen, (5% each) and methane and hydrogen (4% each) in helium were used as standard gas for quantitative calibration, shown in Figure 3.15. Its example chromatogram is shown in Figure 3.16. The operation conditions are column oven temperature of 30 ^{o}C and detector temperature of 70 ^{o}C.

(a)   (b)

Figure 3.14 (a) Shimadzu Gas Chromatography model GC-8A

and (b) C-R8A Chromatopac data processes

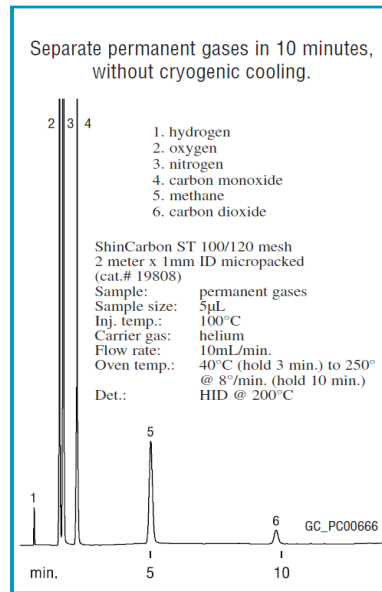Figure 3.15 The Restek pure gases and mixtures standard model Scotty 14

Figure 3.16 Shin Carbon ST Micropacked GC columns

(Restek, 2012)

Standard gas mixture was analyzed and collected by GC. The chromatogram area of product gas composition is converted into mol% by conversion ratio. The conversion ratio defined as equation (3.1). Gas standard composition and conversion ratio were summarized in Table 3.2.

$$Conversion\ ratio = Gas\ standard\ (\%mol)/GC\ area \qquad (3.1)$$

Lower heating values (LHV) of the product gas was defined as the summation of corresponding heating values of H_2, CO and CH_4 (Tendero et al., 2005);

$$LHV = [(25.7 \times H_2) + (30 \times CO) + (85.4 \times CH_4)] \times 4.2 \qquad (3.2)$$

Table 3.2 Gas standard composition and conversion ration

Gas composition	Gas standard (%mol)	Gas standard GC area	Conversion ratio
H2	4	159	0.025157233
O2	5	8808	0.000567666
N2	5	11696	0.000427497
CO	5	8937	0.000559472
CH4	4	6298	0.000635122
CO2	5	9893	0.000505408
He	72	-	-
Total	100	-	-

3.4.3 Product Yields

Gas yield was calculated from the volume of total gas generated and reacted original mass of feedstock as (Lv et al., 2004);

$$Y_{gas} = Q_{total}/m_f \tag{3.3}$$

where, Q_{tatal} is volume of total gas generated (N-m^3) and m_f is original mass of feedstock (kg).

Char yield is defined as the ratio of the mass of obtained char and original mass of feedstock;

$$Y_{char} = (m_{char}/m_f) \times 100\%$$ (3.4)

where, m_{char} is mass of obtained char (kg) and m_f is original mass of feedstock (kg).

3.4.4 Analysis of Fuel Properties

The higher heating value (HHV) of the solid material was calculated from its contents as (Moreno et al., 2012);

$$HHV = 0.491(C) + 0.261(H) - 2.907$$ (3.5)

where, C and H are respective concentrations of carbon and hydrogen (% w/w) in material from ultimate analyses.

3.4.5 Carbon Conversion Efficiency

Carbon conversion efficiency is defined as a ratio between carbon in gaseous fuel and carbon in feedstock;

$$\eta_C = \frac{Q_{gas} \cdot [(CO + CO_2 + CH_4)/100] \cdot (12/22.4)}{m_f \cdot [1 - (A_f/100)] \cdot (C_f/100)} \times 100\%$$ (3.6)

where, Q_{gas} is volume of product gas generated (Nm^3), m_f is original mass of

feedstock (kg), m_{char} is mass of obtained char (kg), A_f is ash content in feedstock (%

w/w) and C_f is carbon content in feedstock (% w/w).

3.4.6 Mass Balance

In this thesis, the mass of feedstock (m_f) was preweighted before every

experiments. The products were gas, solid and liquid. The gas volume (V_{gas}) was

measured by the gas meter. The mass of solid $(m_{solid},$ char) was weight after finish

the process. The mass of liquid (m_{liquid}) was calculated by difference. The mass of

gas product is calculated from the following equation;

$$P_{gas}V_{gas} = m_{gas}RT \qquad (3.7)$$

P_{gas}	=	Pressure of gas products (Pa)
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 plasmochemical process as following equation;

$$m_f = m_{gas} + m_{liquid} + m_{solid} \qquad (3.8)$$

3.4.7 Energy Analysis

In this thesis, energy efficiency was defined as Output energy divided by microwave input energy. Microwave input energy was calculated from microwave input power multiplied by reaction time. Output energy was the energy from gas product. It was calculated from the mass of feedstock (m_f), yield (Y_{gas}) and calorific value (LHV) of product gas. The energy efficiency of plasmochemical conversion was calculated from the following equation;

$$\eta_{energy} = \frac{m_f\,(kg) \times Y_{gas}(m^3/kg)\times LHV(J/m^3)}{microwave\ input\ power\ (W) \times time(s)} \times 100\% \qquad (3.9)$$

3.5 Microwave Plasma Modeling

In this thesis, a computer software was used to simulate the electron density, electron potential and electron temperature in the reaction tube. This particular module solves problems in the general field of plasma, such as RF and microwave plasma.

3.5.1 Model Definition

In this thesis, the microwave plasma reactor was modified from a domestic household microwave oven. The quartz reaction tube was placed at the center of a microwave oven gravity. The oven gravity dimension was symmetric and the waveguide was installed at the center of the gravity wall. Therefore, the two dimensional (2D) geometry can be used for this simulation issue. The 2D geometry of microwave plasma system was imported from the drawing done with the SolidWorks®. The geometry consisted of a reaction tube, a microwave cavity, and a

waveguide. A reaction tube with internal diameter of 27 mm and length of 400 mm was installed vertically at the central of the oven cavity. The oven cavity with wide of 295 mm and high of 180 mm was connected to a rectangular waveguide with wide of 30 mm and high of 43.2 mm. The 2D geometry used for microwave plasma simulation in this thesis was shown in Figure 3.17.
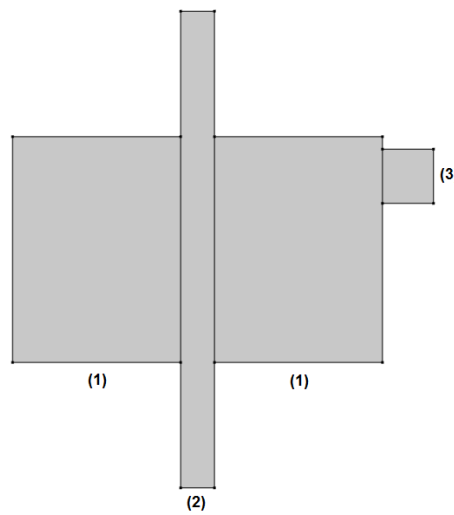
Figure 3.17 The 2D geometry used for microwave plasma simulation

in this thesis, (1) oven cavity, (2) reaction tube, and (3) waveguide

3.5.3 Initial Conditions

Initial conditions needed for this model were microwave operating conditions, materials and plasma gas properties. The microwave power and frequency were 800 W and 2.45 GHz, respectively. The radiation was set as transverse electric mode. The oven cavity and waveguide walls were assigned as a perfect electric conduction material. Argon was chosen as plasma gas. It flow rate was varied in the range of 0.50

to 1.25 lpm. Plasma gas inlet pressure and temperature were fixed at 1 atm and 303.75 K, respectively.

3.5.4 Boundary Conditions

The waveguide and oven cavity walls were assumed to be perfect, lossless metallic walls which were the default boundary condition. The reaction tube wall was set as ground. The start on y- axis of the waveguide was assigned as the rectangular port, where the in-port was the bottommost boundary. The right end of the reaction tube was assigned as plasma gas and ion outflow. For mesh generation, this model uses the default mesh as initial mesh for the adaptive meshing. It is important to initialize the mesh prior to each new solution step. Otherwise, the solver applies the adaptive mesh refinement algorithm on an already adapted mesh. The mesh generated 2D geometry of the inside volume of this system was shown in Figure 3.18.
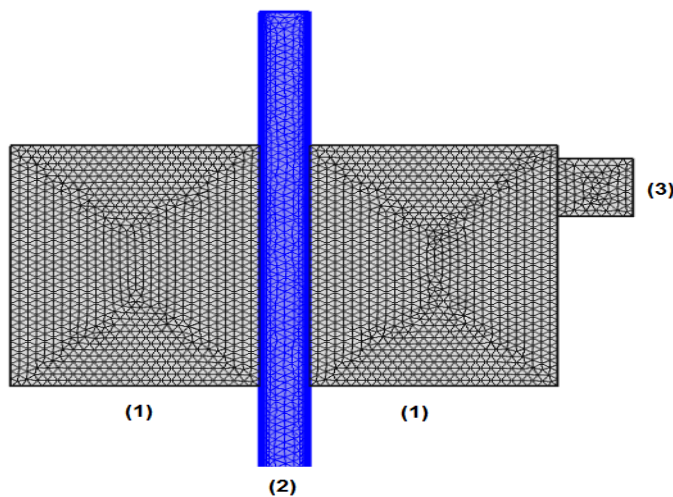

Figure 3.18 The mesh generated 2D geometry of the inside volume of this system, (1) oven cavity, (2) reaction tube, and (3) waveguide

3.6 Thermodynamic Equilibrium Modeling

Plasmochemical reaction in one form of thermal decomposition that uses plasma energy as an external heat source. Thermal decomposition or thermolysis is a chemical decomposition caused by heat. Reactions are usually endothermic and exothermic. Endothermic reaction is chemical reaction that requires energy to break chemical bonds in raw material.

In this thesis, the thermodynamics equilibrium approach was used to determine the product gas composition. The plasma was the external heat source for thermochemical reaction. The assumptions for this model are;

1. Temperature input of thermochemical equilibrium equation is the plasma gas temperature.

2. The thermochemical reactions are only surface reaction.

3. The microwave power is absorbed by carrier gas.

4. The effects of microwave heating are negligible.

The model was run with an elemental composition of feedstock. The feedstock used in the model included waste paper, biomass, and RDF. Product gas compositions were determined by solving nonlinear equations using Newton-Raphson method. Methodology for thermodynamics equilibrium approach are as follow and the modeling diagram was shown in Figure 3.19.

1. Modify thermodynamics equilibrium model of Syed et al., (2012) and gasification model of Jarungthammachote et.al, (2006) and for use in this research.

2. Investigate the chemical reaction of reactant and product with using the modified gasification model.

3. Balance the chemical equation based on elements evolved in the reaction like C, H, O, N and S.

4. Investigate the equilibrium relations for pyrolysis and gasification reactions like water- gas shift, bouduard, and methanation reactions.

5. Solve the obtained the equilibrium constant used a Standard Gibbs function of formation.

6. Solve the obtained system of algebraic equations simultaneously in order to determine the product gas composition and check the errors.

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

$$RMSE = \sqrt{\frac{\sum_i (y_i - x_i)^2}{N}} \qquad (3.10)$$

y_i	=	Value from experiments
x_i	=	Value from model prediction
N	=	Number of data
Subscript i	=	Mole faction value of experiments

8. Modify the model by add constant coefficient to the model for more accuracy.

Start

Plasmochemical Thermodynamics Equilibrium Model in this thesis

- Modified model for this research

$$CH_pO_qN_r + wH_2O = n_{CO}CO + n_{CO_2}CO_2 + n_{CH_4}CH_4 + n_{H_2}H_2 + n_{H_2O}H_2O + \frac{r}{2}N_2$$

$$n_{CO} = x_1, n_{CO_2} = x_2, n_{CH_4} = x_3, n_{H_2} = x_4, n_{H_2O} = x_5$$

Mass balance;

Carbon balance; $\qquad f_1 = x_1 + x_2 + x_3 - 1$

Hydrogen balance; $\qquad f_2 = 4x_3 + 2x_4 + 2x_5 - 2w - p$

Oxygen balance; $\qquad f_3 = x_1 + 2x_2 + x_5 - w - q$

Modify equilibrium constants;

Modified boudouard reaction; $\qquad f_4 = K_1 \cdot (x_2)(x_{total}) - (x_1)^2$

Modified water-gas shift reaction; $f_5 = K_2(x_1)(x_5) - (x_2)(x_4)$

Solving K_1 and K_2 by input temperature in following equation;

$$\ln(K_i) = -\frac{\Delta G_T^O}{RT}$$

$$\Delta G_T^O = \sum_i v_i \cdot \Delta g_{f,T,i}^O$$

$$\Delta g_{f,T}^O = h_f^O - a'T\ln(T) - b'T^2 - \left(\frac{c'}{2}\right)T^3 - \left(\frac{d'}{3}\right)T^4 + \left(\frac{e'}{2T}\right) + f' + g'T$$

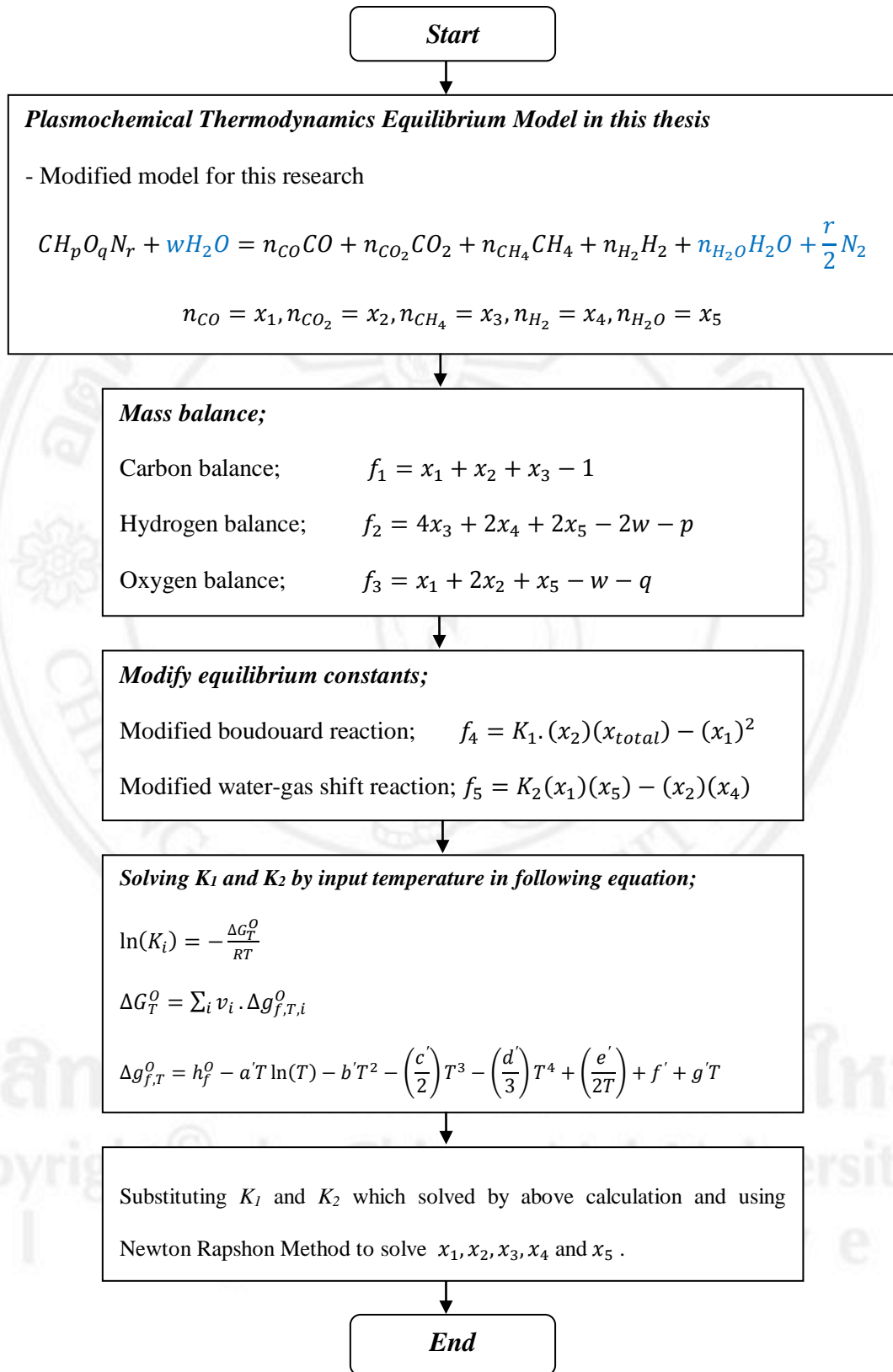Substituting K_1 and K_2 which solved by above calculation and using Newton Rapshon Method to solve x_1, x_2, x_3, x_4 and x_5.

End

Figure 3.19 Thermodynamics equilibrium modeling diagram