CHAPTER 2

THEORY

2.1 Refuse Derived Fuel

Waste to Energy (WTE) is an extremely attractive option. It refers to any waste treatment that generates the energy in the form of electricity or heat from a waste source as well as energy byproducts, such as synthesis gas, liquid fuel and char. Presently, WTE technologies consist of many conversion methods, such as physical, thermochemical and biochemical. Physical conversion is a basic technology involving various processes to improve physical properties of waste. Hazardous waste, metal and other incombustible matters can be removed. The remaining combustible fraction of the waste is subsequently dried, size-reduced and compacted into fuel pellets. Refuse derived fuel (RDF) is the main product from the physical conversion process as. RDF is combustible or, in other word, high calorific fraction recovered from MSW. There is another definition, defined by ASTM standard (2006) that RDF is a shredded fuel derived from MSW which metal, glass and other inorganic materials have been removed and has particle size 95 %wt passes through a 2-in square mesh screen. MSW composition is varied from different sources, seasons and living behaviors. Raw MSW has high moisture content, low calorific value, wide range of particle size distribution and high ash content. These reasons make using raw MSW as fuel difficult and unattractive.

RDF presents several advantages as a fuel over raw MSW. The main advantages are higher calorific value which also remains fairly constant, more uniformity of physical and chemical composition, ease of storage, handling and transportation, lower pollutant emissions and reduction of excess air requirement during combustion (Nithikul et al., 2007). In low and middle-income countries, composition of the mechanically separated MSW consists of 30% paper, 50% biomass, and 20% plastic (Chandrappa, 2012).

Based on ASTM standards E856-83 (2006), RDF can be classified into 7 categories. Classification of RDF were summarized in Table 2.1. RDF should have high calorific value and low concentration of toxic chemicals specifically for chlorine, heavy metals and other hazardous components . Although there is no RDF quality regulation in Asia right now. The quality standards for RDF and the elemental composition of in Europe were shown in Tables 2.2 and 2.3, respectively.

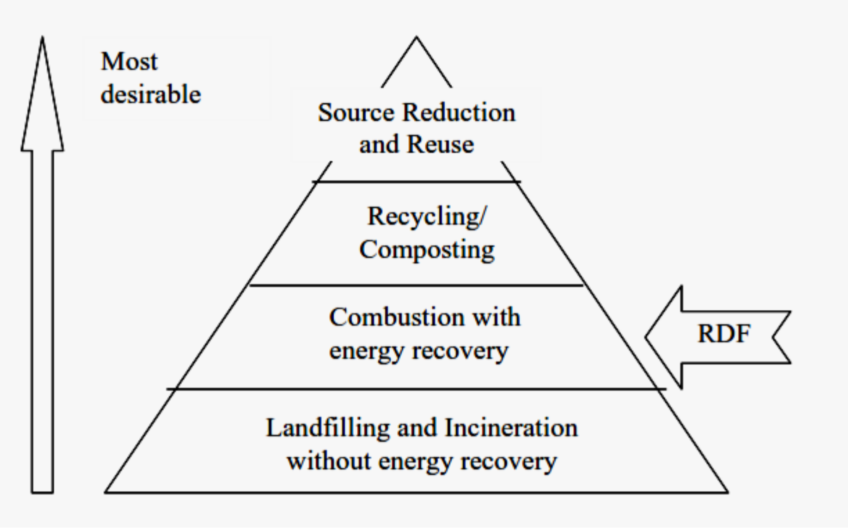

Figure 2.1 Integrated MSW hierarchy

(Source; Nithikul et al., 2007)

Table 2.1 Classification of RDF (Source; Nithikul et al., 2007)

Classification	Definition
RDF 1	Wastes used in as discarded form
RDF 2	Wastes processed to coarse particle size with or without ferrous metal separation such that 95% by weight passes through a 6 in square mesh screen, namely Coarse RDF
RDF 3	Wastes processed to separate glass, metal and inorganic materials, shredded such that 95 % by weight passes 2 in square mesh screen, namely Fluff RDF
RDF 4	Combustible wastes processed into powder form, 95 %wt passes through a 10 mesh screen (0.035 in square), namely Powder RDF
RDF 5	Combustible wastes densified (compressed) into the form of pellets, slugs, cubettes or briquettes, namely Densified RDF, as Figure 2.2.
RDF 6	Combustible wastes processed into liquid fuels, namely RDF slurry
RDF 7	Combustible wastes processed into gaseous fuels, namely RDF syngas

Figure 2.2 RDF 5 or Densified RDF

(Source; http://renovables.livejournal.com/4535.html)

Table 2.2 Standard quality of RDF (Source; Nithikul et al., 2007)

Parameters	Finland[a]	Italy	UK
Calorific Value (MJ/kg)	13-16	15	18.70
Moisture content (%wt)	25-35	< 25	7-28[b]
Ash content (%wt)	5-10	20	12.00
Sulfur (%wt)	0.1-0.2	0.60	0.1-0.5
Chlorine (%wt)	0.3-1.0	0.90	0.3-1.2

[a] Restriction for household wastes

[b] 7 for Densified-RDF and 28 for Coarse-RDF

Table 2.3 Elemental composition of RDF (Source; Nithikul et al., 2007)

RDF components (%wt)	C	H	O	N	S	Cl	H_2O	Ash
Paper	34.4	4.72	32.4	0.16	0.21	0.24	21	4.62
Plastic	56.4	7.79	8.05	0.85	0.29	3.00	15	8.59
Wood	41.2	5.03	34.5	0.02	0.07	0.09	16	2.82
Textile	37.2	5.02	27.1	3.1	0.28	0.27	25	1.98
Leather, Rubber	43.1	5.37	11.6	1.34	1.17	4.97	10	22.5

2.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was defined by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) (Wongsiriamnuay, 2012). TGA is the chemical analysis of mass changes on material. It is used to determine moisture content, volatile matter, fixed carbon, and ash. This technique can be used in a complete evaluation and interpretation of results. The material is heated to observe the mass change as a function of temperature and time. The temperature was controlled as isothermal or non-isothermal. Mass change is plotted against temperature or time. The mass loss appears as a step when increasing temperature. TGA may see three processes under an inert atmosphere, (i) drying process, (ii) volatile process, and (iii) carbonization process. Drying process is to decrease a moisture from material. Material is normally heated from 50 to 135 ºC with heating rate of 10 ºC/min under nitrogen environment and held the temperature of 135 ºC for 5 min. Volatile process is to drive out a volatile component in a material. Material is normally heated from 135 to 900 ºC with heating rate of 100 ºC/min under nitrogen environment. Carbonization process is a term for the conversion of an organic substance into carbon or a carbon-containing residue. This process occurs at reaction temperature of 900 ºC where it is held for 20 min. Process reactions can be detected by coupling thermogravimetric analyzer with differential scanning calorimeter (DSC), fourier transform infrared spectrometer (FT-IR) and mass spectrometer (MS) (Wongsiriamnuay, 2012).

TGA process are isothermal and non-isothermal reaction. Reaction kinetics of non-isothermal behavior are analyzed to determine apparent activation energy and pre-exponential factor for thermal degradation. Thermal decomposition behavior of material under nitrogen, air, and oxygen environment can be obtained. The TGA results are summarized as conversion (α) and defined by the following equation (Wongsiriamnuay, 2012);

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \tag{2.1}$$

where, W_i is initial mass of the raw material, W_t is the mass of oxidized material, and W_f is the mass of final residual. The general non-isothermal decomposition reaction rate is defined as (Wongsiriamnuay, 2012);

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2.2}$$

Hence;

$$k = Ae^{-\left(E/_{RT}\right)} \tag{2.3}$$

where, k is Arrhenius equation states, T is the temperature, A is the pre-exponential or frequency factor, t is the time, E is the activation energy, R is the universal gas constant in molar, n is the order of reaction. Equation (2.2) and (2.3) can be summarized in logarithmic form as (Wongsiriamnuay, 2012);

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1-\alpha) - \frac{E}{RT} \tag{2.4}$$

2.3 Microwave Plasma Generation

Microwave radiation is the electromagnetic wave lies within the range between infrared and radio frequency. The frequencies of microwave are in the range of 0.3 to 300 GHz, with wave lengths ranging from 1 mm up to 1 m. It is used in many industry and household as a source thermal energy (Rattanadecho and klinbun, 2011). Household microwave ovens mainly operate at a frequency of 2.45 GHz and corresponds to wavelength of 12.2 cm. To generate plasma, microwaves are guided along the system and transmitted energy and electric field to the plasma gas electrons. Elastic collisions between electrons and heavy particles occur. Due to the large mass of heavy particles, the collided electrons rebound whereas the heavy particles remain static. Supposing that electric field exceeds the breakdown voltage or dielectric strength of the carrier gas or electrons get enough energy to produce inelastic exciting or even ionizing collisions, the gas is partially ionized and becomes plasma which supports microwave propagation. Plasmas are usually formed at the tip of electrode or igniter. Hence, the sharp metal object of electrode or igniter that help focusing the energy of the supplied electric field to the level which is enough to generate the plasma may be employed. Plasmas are produced through the inductive transfer of energy from standing waves in suitable resonator structures (Tendero et al., 2006; Chakartnarodom, 2008). The breakdown voltage of some gases which usually use as plasma gas relative to N_2 are listed in Table 2.4. The maximum breakdown voltage of N_2 is 3.1 kV/mm.

Table 2.4 Breakdown voltage of some plasma gases relative to N_2

Gas	Relative Breakdown Voltage
CO	1.05
N_2	1.00
Air	0.97
O_2	0.92
H_2	0.50
Ar	0.18

(Source; Chakartnarodom, 2008)

The electric field ($\vec{E}$) perpendicular to the metal surface is calculated by the following equation;

$$(\vec{E} = -4\pi\vec{P}) \tag{2.5}$$

where, $\vec{P}$ is polarization vector. The polarization results from the motion of electrons within the conductor in response to the microwave field oscillations (Chakartnarodom, 2008). Polarization vector ($\vec{P}$) is calculated by;

$$(\vec{P} = ne\vec{X}) \tag{2.6}$$

where, $\vec{X}$ is the displacement vector of the electrons, e is the charge of an electron, and n is the number of electrons (Chakartnarodom, 2008).

The microwave plasma source can be the same magnetron as the one used in a typical household microwave oven. It is simple, compact, and economical. Applications of the microwave plasma source, it is very important to effectively utilize electrons, ions, free radicals, and other molecular species inside the plasma flame.

In the case of plasmochemical conversion of solid waste, the high density plasma provides a suitable condition to dissociate and ionize waste molecules in the abatement system, to decompose and burn out chemical and biological warfare agents, and to atomize and synthesis fuel gas. All microwave systems work according to the same principle. Microwave plasma sources consist of the following equipments;

2.3.1 Microwave Power Source

Microwave power source includes an electric power supply, a magnetron and a circulator. Electrical supply in the microwave system is from a high voltage transformer. It supplies electrical energy to the magnetron. For the microwave plasma system, wide range of power is used, such as 250 W (Kim et al., 2010; Chaichumporn et al., 2011), 800 W (Khongkrapan et al., 2012), 2 kW (Wang et al., 2012), 4 kW (Hong et al., 2012) etc. The magnetron is used as a microwave generator equipment. It generates microwaves using the interaction of a stream of electrons with a magnetic field. The resonant cavity magnetron tube was created by John Randall and Harry Boot in 1940. To generates microwaves, the high voltage is applied to a cathode magnetron and a strong magnetic field is applied across the device. The electrons emitted at the cathode take a spiral course and a vortex is created at each cavity. The copper anode begins to resonate and produces the radiated microwave pulse (The Magnetron, 2009). The magnetron is a fairly efficient device. For the magnetron used in a domestic microwave oven (Figure 2.3), 1100 W electrical input power would be generally created about 700 W of microwave power output with an efficiency of around 65% (Turner, 1976). Circulator as Figure 2.4 is the equipment which protects the magnetron from the reflected microwave power. The microwave is applied to a port of circulator and transmitted to the next port in only rotation mode. For example, a three-port circulator, the microwave that applied to port 1 would only come out of port 2, the microwave that applied to port 2 would only come out of port 3 and the microwave that applied to port 3 would only come out of port 1 (Wenzel, 1991). This is to protect the magnetron from reflected microwave power.

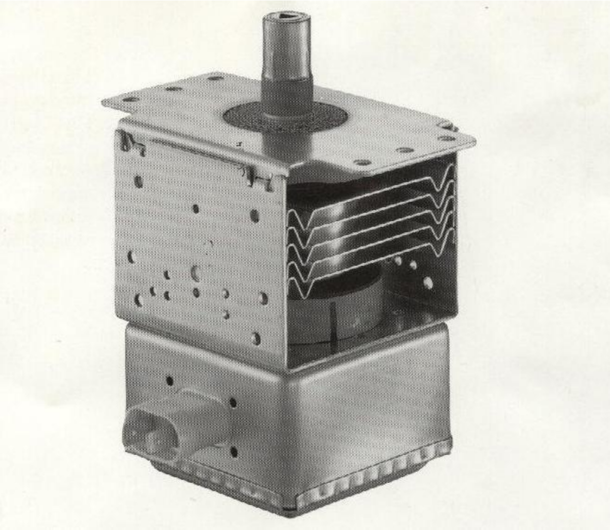

Figure 2.3 Magnetron of domestic microwave oven

(source; http://njhighhope.en.alibaba.com/product/210766981-200271897/Magnetron_Electron_Tube_2M210.html)

Figure 2.4 Microwave circulator

(source; http://www.meslmicrowave.com/isolators-and-circulators/waveguide/)

2.3.2 Microwave Equipment

Microwave equipments include waveguides and a tuning system. A waveguide as shown in Figure 2.5 is the equipment which transfers microwave to the designed direction. It is essentially coaxial lines without center conductors. Waveguides can be made for a several microwave frequencies. The magnetron of a household microwave oven generates microwave with frequency of 2.45 GHz. The D-band frequency of 2.20 to 3.30 GHz, the WR-340 rectangular waveguide with high of 43.2 mm and wide of 86.4 mm is usually used to transfer the wave with this frequency range (COBHAM Inc.). Tuning system is the equipment that uses to optimizes microwave power concentration, such as three-stub tuner and tuning plunger as Figures 2.6 and 2.7, respectively. A 3-stub tuner is used for impedance matching by progressively inserting each metallic stub into the waveguide (Chaichumporn et al., 2011). Plunger is used to reflect microwave power at the end of waveguide where boundary conditions are required for the electric field to be zero. It creates superposition of incident and reflected waves to form a standing wave pattern with a maximum centered at the plasma zone (Gower, 2001; Chaichumporn et al., 2011).

Figure 2.5 Microwave waveguide

(Source; http://www.microwaveengservices.com/Webpage/waveguide.html)

Figure 2.6 A 3-stub tuner

(Source; http://www.hueray.cn/en/productread.asp?id=32)

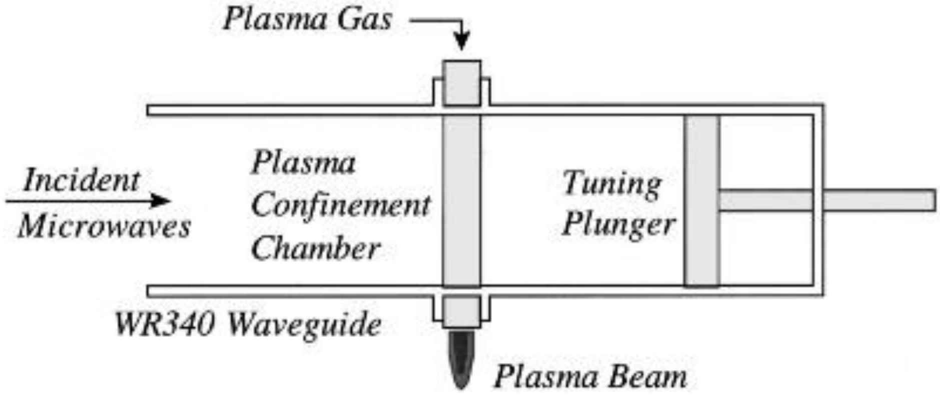

Figure 2.7 Microwave tuning plunger

(Source; Gower, 2001)

In this thesis, the microwave plasma reactor is modified from a domestic microwave oven. The oven is included a waveguide with metal bump which acted as circulator. Microwave is passed through waveguide and circulated in oven gravity and cannot get reflected to the magnetron.

2.3.3 Plasma Reactor

Plasma reactor includes a reaction tube, a nozzle, an ignition system, and a gas injection system. The reaction tube is usually made of quartz (Kim et al., 2010; Chaichumporn et al., 2011; Khongkrapan et al., 2012; Wang et al., 2012; Hong et al., 2012) or ceramic in order to operating at high temperature. To startup plasma, many researchers used an ignition system, such as sharp metal, to help focusing the energy of the supplied electric field to the level that is enough to generate the plasma (Chaichumporn et al., 2011; Khongkrapan et al., 2012).

2.4 Plasmochemical Reaction

Plasmochemical reaction is the kind of thermochemical reaction which uses energy from the plasma to decompose chemical bonds in raw material. There are many kinds of chemical reactions occurring within the plasma such as excitation reaction, and ionization reaction. The possible chemical reactions in the plasma and ionization energy can be summarized as following (Chakartnarodom, 2008);

- **Atomic and Molecular reactions**

Penning dissociation; $M^* + A_2 \rightarrow 2A + M$ (2.7)

Penning ionization; $M^* + A \rightarrow A^+ + M + e$ (2.8)

Charge transfer; $A^\pm + B \rightarrow B^\pm + A$ (2.9)

Ion recombination; $A^- + B^+ \rightarrow AB$ (2.10)

Neutral recombination; $A + B + M \rightarrow AB + M$ (2.11)

- **Decomposition**

Electron; $e + AB \rightarrow A + B + e$ (2.12)

Atomic; $A^{*} + B_2 \rightarrow AB + B$ (2.13)

- **Synthesis**

Electron; $e + A \rightarrow A^{*} + e$ (2.14)

$A^{*} + B \rightarrow AB$ (2.15)

Atomic; $A + B \rightarrow AB$ (2.16)

where, A, B, and M are atom or molecule of gas, e is an electron. The asterisk denotes an atom/molecule in an excited state.

Ionization energy of an atom or molecule describes the amount of energy required to remove an electron from the atom or molecule in the gaseous state. It is typically specified in electron volts (eV). Plasma is referred to an ionized gas that releases an energy in the form of heat, light, and sound. To generate plasma, energy applied to plasma gas must be more than or equal to the first ionization energy of the plasma gas. Ionization energy of some gases is summarized in Table 2.5.

Table 2.5 Ionization energy of several molecules

Molecule	Ionization Energy (eV)
CO/CO^+	14.0
CO_2/CO_2^+	13.8
CH_4/CH_4^+	12.7
H_2/H_2^+	15.4
H_2O/H_2O^+	12.6
N_2/N_2^+	15.6
O_2/O_2^+	12.2
Ar/Ar^+	15.8

(Source; Chakartnarodom, 2008)

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. Example endothermic reactions are boudouard, water-gas, and steam methane reforming reactions. Water-gas reactions are endothermic which required energy and water (H_2O). Hydrogen (H) molecules in system can be from moisture or steam. Carbon (C) and hydrogen (H) molecules in the raw material need to have enough energy to transform into carbon monoxide (CO) and hydrogen (H_2) as equation (2.17), or carbon dioxide (CO_2) and hydrogen (H_2) as equation (2.18), respectively. Boudouard reaction is endothermic which required energy and carbon dioxide. Carbon (C) molecules in the raw material and oxygen (O) molecules in carbon dioxide have enough energy and transformed into carbon monoxide (CO) as equation (2.19). Steam methane reforming is endothermic reaction which required energy and water (H_2O) to decomposes methane (CH_4) into carbon monoxide (CO) and hydrogen (H_2) as equation (2.20), or carbon dioxide (CO_2) and hydrogen (H_2) as equation (2.21), respectively.

- **Endothermic reactions**

Water-gas reaction;

$$C + H_2O \rightarrow CO + H_2 \qquad \text{+118 kJ/mol} \qquad (2.17)$$

$$C + 2H_2O \rightarrow CO_2 + H_2 \qquad \text{+76 kJ/mol} \qquad (2.18)$$

Boudouard reaction;

$$C + CO_2 \rightarrow 2CO \qquad \text{+161 kJ/mol} \qquad (2.19)$$

Steam methane reforming reaction;

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{+206 kJ/mol} \qquad (2.20)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \text{+165 kJ/mol} \qquad (2.21)$$

Exothermic reaction is chemical reaction that releases energy from the system in the form of heat, light, electricity, and sound. Example exothermic reaction are water-gas shift, partial and complete oxidation reactions. Oxidation reactions (combustion) are exothermic which required oxygen (O_2). Carbon (C) and hydrogen (H) molecules in the raw material are oxidized and transformed into carbon monoxide (CO) as equation (2.22), or carbon dioxide (CO_2) and water (H_2O) as equation (2.23) and (2.24), respectively. Ash is also produced during combustion, as a result of non-combustible inorganic compounds. The products from this phase enter the last phase where, these are subjected to reduction processes and still combustible gases such as carbon monoxide and hydrogen are produced. Energy from this process can be obtained from oxidation. In distillation, the heavier biomass molecules are converted into lighter organic molecules and carbon monoxide (Wongsiriamnuay, 2012).

- **Exothermic reactions**

Partial oxidation reaction;

$$2C + O_2 \rightarrow 2CO \qquad -246 \text{ kJ/mol} \qquad (2.22)$$

Complete oxidation reaction;

$$C + O_2 \rightarrow CO_2 \qquad -409 \text{ kJ/mol} \qquad (2.23)$$

$$H_2 + \left(\frac{1}{2}\right) O_2 \rightarrow H_2O \qquad -242 \text{ kJ/mol} \qquad (2.24)$$

Water-gas shift reaction;

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{-42 kJ/mol} \qquad (2.25)$$

2.5 Microwave Plasma Modeling

In this thesis, a computer software is used to simulate the electric field and the power concentration in the microwave system. This particular module solves problems in the general field of electromagnetic waves, such as RF and microwave applications. Modeling microwave plasmas involves solving equations for the electron density, mean electron energy, heavy species, the electrostatic potential, and the high frequency electric field. The high frequency electric field is calculated in the frequency domain and losses are introduced via a complex plasma conductivity. Microwave plasma model is used to calculate electromagnetic field and energy in plasma zone. The model is used to make sure that electron can gain enough energy from the electromagnetic wave. The physics of a microwave plasma is certainly different depending on whether the TE mode (out-of-plane electric field) or the TM mode (in-plane electric field) is propagating. In neither case, it is possible for the electromagnetic wave to penetrate into regions of the plasma where the electron density exceeds the critical electron density.

2.5.1 Governing Equations

Maxwell’s equations are solved to determine electric field distribution in a microwave cavity as follows (Salvi et al., 2010);

$$\nabla \times \left(\frac{1}{\mu'} \nabla \times \vec{E}\right) - \frac{\omega^2}{c}\left(\varepsilon' - i\varepsilon''\right)\vec{E} = 0 \qquad (2.26)$$

where, $\vec{E}$ is electric field intensity (V/m), ε' is relative permittivity or dielectric constant of a material, ε'' is relative dielectric loss of a material, ω is angular wave frequency (rad/s), μ' is relative permeability of a material and c is speed of light in free space (3x10^8 m/s).

Electromagnetic field inside a rectangular waveguide, Maxwell's equations governing the electromagnetic field are expressed in terms of the electric field (E) and magnetic field (H). In the Cartesian coordinate system (X, Y, Z), they are given in TE_{10} mode as (Klinbun and Rattanadecho, 2012);

$$E_X = E_Z = H_Y = 0 \qquad (2.27)$$

$$\frac{\partial E_Y}{\partial t} = \frac{1}{\varepsilon}\left(\frac{\partial H_X}{\partial Z} - \frac{\partial H_Z}{\partial X} - \sigma E_Y\right) \qquad (2.28)$$

$$\frac{\partial H_Z}{\partial t} = -\frac{1}{\mu}\frac{\partial E_Y}{\partial X} \qquad (2.29)$$

$$\frac{\partial H_X}{\partial t} = \frac{1}{\mu}\frac{\partial E_Y}{\partial Z} \qquad (2.30)$$

where, $\varepsilon = \varepsilon_0\varepsilon_r$ is the electrical permittivity, σ is the electrical conductivity and $\mu = \mu_0\mu_r$ is the magnetic permeability.

The electric field intensity obtained from above equation and material properties are required to calculate the volumetric power generation due to microwave exposure by using the following equation (Salvi et al., 2010);

$$Q = \sigma\left|\vec{E}\right|^2 = 2\pi\varepsilon_0\varepsilon'' f\left|\vec{E}\right|^2 \tag{2.31}$$

where, σ is electrical conductivity of a material (s/m), ε_0 is free space permittivity (8.854x10^{-12} F/m), and f is frequency (Hz).

2.5.2 Domain Equation

The electron density and mean electron energy are calculated by solving drift-diffusion equations. The electron density is given by the following equation;

$$R_e = \frac{\partial}{\partial t}(n_e) + \nabla.\left[-n_e(\mu_e.E) - D_e.\nabla n_e\right] \tag{2.32}$$

where, R_e is the electron rate expression (1/m^3·s) , n_e is the electron density (1/m^3), μ_e is the electron mobility which is either a scalar or tensor (m^2/V·s), E is the electric field (V/m), and D_e is the electron diffusivity which is either a scalar or a tensor (m^2/s). The electron energy is given by the following equation;

$$R_\varepsilon = \frac{\partial}{\partial t}(n_\varepsilon) + \nabla.\left[-n_\varepsilon(\mu_\varepsilon.E) - D_\varepsilon.\nabla n_\varepsilon\right] + E.\Gamma_e \tag{2.33}$$

$$\Gamma_e = \left[-n_e(\mu_e.E) - D_e.\nabla n_e\right] \tag{2.34}$$

where, ,R_ε is the energy loss or gain due to inelastic collisions (V/m^3·s), n_ε is the electron density (1/m^3), $\mu_\varepsilon$is the electron mobility which is either a scalar or tensor (m^2/V·s), E is the electric field (V/m), and D_ε is the electron energy diffusivity which is either a scalar or a tensor (m^2/s). The electron diffusivity (D_e), electron energy diffusivity (D_ε) are calculated from the following equation;

$$D_e = \mu_e . T_e \tag{2.35}$$

$$D_\varepsilon = \mu_\varepsilon . T_e \tag{2.36}$$

$$\mu_\varepsilon = \left(\frac{5}{3}\right) . \mu_e \tag{2.37}$$

where, T_e is the electron temperature (V). The electron temperature (T_e) is calculated from following equation;

$$T_e = \left(\frac{2}{3}\right) . \bar{\varepsilon} \tag{2.38}$$

where, $\bar{\varepsilon}$ is the mean electron energy (V). The mean electron energy ($\bar{\varepsilon}$) is calculated from following equation;

$$\bar{\varepsilon} = \frac{n_\varepsilon}{n_e} \tag{2.39}$$

In a microwave reactor, the high frequency electric field is calculated in the frequency domain using the following equation;

$$\nabla \times (\mu_r^{-1} \nabla \times E) - k_0^2 \left(\varepsilon_r - \frac{j\sigma}{\omega \varepsilon_0} \right) E = 0 \tag{2.40}$$

where, μ_r is the relative permeability, ω is the angular frequency, σ is the conductivity, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity, and k_0 is the free space wave number, respectively. Losses are assumed to be zero everywhere.

2.6 Plasmochemical Thermodynamic Equilibrium Modeling

A model prediction of product gas composition using elemental analysis of raw material is helpful. There are many thermodynamic equilibrium models that can be used to predict product gas composition from plasmochemical process. It can apply to various raw material and reactor types with reasonable accuracy. The product gas composition from thermodynamic equilibrium modeling provides a closer prediction when the reaction temperature is sufficiently high (Wongsiriamnuay, 2012).

Plasmochemical modeling is the relations of thermodynamic and chemical equilibrium. Thermodynamic equilibrium is thermal balance of system. Chemical equilibrium is the state of minimum Gibbs free energy and maximum system entropy. Modeling results can be used as the maximum limit on product gas composition (Syed et al., 2012).

The empirical model, thermodynamic and chemical equilibrium relations are used to calculate the composition of the product gas. It can be used for any type of thermochemical process, such as pyrolysis, gasification as well as plasmochemical conversion. There are various factors affecting product gas composition such as raw material properties, and operating parameters. In this thesis, the model is based on the following assumptions;

1.The plasmochemical system is assumed to be adiabatic. There is no heat and work transferred. The reaction occurred under auto-thermal processes.

2. Raw materials have low content of ash and tar.

3. All carbon content in raw materials is fully converted into gas and there is sufficient residence time to achieve thermodynamic equilibrium.

4.The product gas from plasmochemical process are CO, CO_2, CH_4, H_2, and H_2O. All gases are ideal. Other gases, liquid, and solid residual are not present.

5. There is no oxygen in a product and no free oxygen content to react with other product in secondary reaction step.

The plasmochemical thermodynamics equilibrium model in thesis is modified from the thermodynamics equilibrium model of Syed et al., (2012) as equation (2.41) and gasification model of Jarungthammachote et al., (2006) as equation (2.42).

$$CH_xO_yN_z + m(O_2 + 3.76N_2) = x_1H_2 + x_2CO + x_3CO_2 + x_4H_2O + x_5CH_4 + x_6\mathrm{C} + \left(\frac{z}{2} + 3.76m\right)N_2 \tag{2.41}$$

$$CH_xO_yN_z + wH_2O + m(O_2 + 3.76N_2) = n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{CH_4}CH_4 + n_{H_2O}H_2O + \left(\frac{z}{2} + 3.76m\right)N_2 \tag{2.42}$$

The equilibrium model in this thesis is formed as;

$$CH_pO_qN_r + wH_2O = n_{CO}CO + n_{CO_2}CO_2 + n_{CH_4}CH_4 + n_{H_2}H_2 + n_{H_2O}H_2O + \frac{r}{2}N_2 \quad (2.43)$$

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

Hence, equation (2.43) can be written as;

$$CH_pO_qN_r + wH_2O = x_1CO + x_2CO_2 + x_3CH_4 + x_4H_2 + x_5H_2O + \frac{r}{2}N_2 \quad (2.44)$$

The water content (w in equation (2.44)) of raw material is defined as;

$$w = M \times mc/18.015 \times (1 - mc) \quad (2.45)$$

where, mc is moisture content in raw material (%) and M is calculated from following equation;

$$M = (12.0107 \times nC) + (1.0079 \times nH) + (15.994 \times nO) \quad (2.46)$$

To calculate the value of five unknowns, five equations are required. Followings are the mass balances of each element; carbon balance as equation (2.47), hydrogen balance as equation (2.49), and oxygen balance as equation (2.51). Three equations can be derived by the conservation of elemental mass present in the reactants and products as the equations (2.48), (2.50), and (2.52).

- Carbon balance; $n_{CO} + n_{CO_2} + n_{CH_4} - 1 = 0$ (2.47)

  Hence; $f_1 = x_1 + x_2 + x_3 - 1$ (2.48)

- Hydrogen balance; $4n_{CH_4} + 2n_{H_2} + 2n_{H_2O} - 2w - p = 0$ (2.49)

  Hence; $f_2 = 4x_3 + 2x_4 + 2x_5 - 2w - p$ (2.50)

- Oxygen balance; $n_{CO} + 2n_{CO_2} + n_{H_2O} - w - q = 0$ (2.51)

  Hence; $f_3 = x_1 + 2x_2 + x_5 - w - q$ (2.52)

Two more equations are required to be solved together with equations (2.48), (2.50), and (2.52) to calculate the equilibrium composition of product gas. These equations are derived using the equilibrium constants of elementary reactions.

- Boudouard reaction; $C + CO_2 = 2CO$ (2.53)

- Water-gas shift reaction; $CO + H_2O = CO_2 + H_2$ (2.54)

Therefore, the equilibrium constant is written for equations (2.53) and (2.54) as follows;

- The equilibrium constant for boudouard reaction (Syed et al., 2012);

$$K_1 = \prod_l (x_i)^{v_i}(P/P^O)^{\Sigma_i v_i} = \frac{(n_{CO})^2}{(n_{CO_2})(n_{total})} \tag{2.55}$$

$$K_1 = \prod_l (x_i)^{v_i}(P/P^O)^{\Sigma_i v_i} = \frac{(x_1)^2}{(x_2)(x_{total})} \tag{2.56}$$

- The equilibrium constant for water-gas shift reaction (Wongsiriamnuay, 2012);

$$K_2 = \prod_l (x_i)^{v_i}(P/P^O)^{\Sigma_i v_i} = \frac{(n_{CO_2})(n_{H_2})}{(n_{CO})(n_{H_2O})} \tag{2.57}$$

$$K_2 = \prod_l (x_i)^{v_i}(P/P^O)^{\Sigma_i v_i} = \frac{(x_2)(x_4)}{(x_1)(x_5)} \tag{2.58}$$

$$n_{total} = n_{CO} + n_{CO_2} + n_{CH_4} + n_{H_2} + n_{H_2O} \tag{2.59}$$

Hence;

$$x_{total} = x_1 + x_2 + x_3 + x_4 + x_5 \tag{2.60}$$

where, x_i is mole fraction of species *i* in the ideal gas mixture, *v* is stoichiometric number (positive value for products and negative value for reactants), and P^O is standard pressure (1 atm). The equilibrium constants from equation (2.56) and (2.58) can be modified as equation (2.62) and (2.64) that enable to complete the five equations required to calculate the equilibrium composition of product gas.

- Modified boudouard reaction can be written as;

$$f_4 = K_1.\left(n_{CO_2}\right)(n_{total}) - (n_{CO})^2 = 0 \qquad (2.61)$$

Hence; $$f_4 = K_1.(x_2)(x_{total}) - (x_1)^2 = 0 \qquad (2.62)$$

- Modified water-gas shift reaction can be written as;

$$f_5 = K_2(n_{CO})\left(n_{H_2O}\right) - \left(n_{CO_2}\right)\left(n_{H_2}\right) \qquad (2.63)$$

Hence; $$f_5 = K_2(x_1)(x_5) - (x_2)(x_4) \qquad (2.64)$$

The value of equilibrium constants *K₁* and *K₂* are found at constant temperature and pressure using the standard state Gibbs function of change (ΔG_T^O).

$$\ln(K_i) = -\frac{\Delta G_T^O}{RT} \qquad (2.65)$$

$$\Delta G_T^O = \sum_i v_i \,.\, \Delta g_{f,T,i}^O \qquad (2.66)$$

where, R is the universal gas constant (R=8.314 kJ.kmol^{-1}.K^{-1}), T is the absolute temperature in Kelvin, ΔG^{O}_{T} is the standard Gibbs function of reaction, $\Delta g^{O}_{f,T,i}$ represents the standard Gibbs function of formation at given temperature T of the gas species i, and v_i is stoichiometric number of gases species i involving reaction. Sign convention for stoichiometric number is always a plus sign (+) for product. For reactants, the value of the term will be negative (-).

A standard Gibbs function ($\Delta g^{O}_{f,T,i}$) of formation of CO, CO_2, CH_4, and H_2O at any temperature can be calculated using the following equation;

$$\Delta g^{O}_{f,T} = h^{O}_{f} - a'T\ln(T) - b'T^{2} - \left(\frac{c'}{2}\right)T^{3} - \left(\frac{d'}{3}\right)T^{4} + \left(\frac{e'}{2T}\right) + f' + g'T \qquad (2.67)$$

where, $a', b', c', d', e', f'\, and\ g'$ are the coefficients of empirical equation, and h^{O}_{f} is the enthalpy of formation of gases, are presented in Table. 2.6.

The value of ΔG^{O}_{T} is calculated by taken the species present in the relevant elementary reactions. The value of ΔG^{O}_{T} for boudouard and methanation reaction are formulated as;

- ΔG^{O}_{T} for boudouard reaction (Syed et al., 2012);

$$\Delta G^{O}_{T} = 2\Delta g^{O}_{f,CO} - \Delta g^{O}_{f,CO_2} \qquad (2.68)$$

- ΔG_T^O for water-gas shift reaction (Wongsiriamnuay, 2012);

$$\Delta G_T^O = \Delta g_{f,CO_2}^O - \Delta g_{f,H_2O}^O - \Delta g_{f,CO}^O \qquad (2.69)$$

Substituting K_1 and K_2 to solve above calculation in (2.62) and (2.64), Newton Rapshon Method is then used to solve for $n_{CO}, n_{CO_2}, n_{CH_4}, n_{H_2}$ and n_{H_2O}.

Table 2.6 The value of $\boldsymbol{h_f^O}$ (kJ/kmol) and coefficients of empirical equation for $\Delta \boldsymbol{g_{f,T}^O}$ (Source; Syed et al., 2012)

Compound	h_f^O	a' (x10^{-3})	b' (x10^{-6})	c' (x10^{-9})	d' (x10^{-12})	e' (x10^{2})	f' (x10^{-1})	g' (x10^{-2})
CO	-110.5	5.619	-11.900	6.383	-1.846	-4.891	8.684	-6.131
CO_2	-393.5	-19.490	31.220	-24.480	6.946	-4.891	52.700	-12.070
CH_4	-74.8	-46.200	11.300	13.190	-6.647	-4.891	141.100	-22.340
H_2O	-241.8	-8.950	-3.672	5.209	-1.478	0.000	28.680	-1.722