CHAPTER 4

PYROLYSIS MODEL DEVELOPMENT

During pyrolysis, chemical reactions and heat transfer processes occur. The reactions involved in pyrolysis are complex and proceed through a complex series of concurrent and consecutive chemical reactions. These reactions can be both endothermic and exothermic. In pyrolysis, the solid may be heated by conduction, convection and/or radiation. Within the solid, this heat moves forward by conduction which proceeds pyrolysis.

Under these conditions both temperature and rate of pyrolysis will be function of distance into the solid and of time. In order to simplify the analysis and evaluation of pyrolysis parameters, it has been common practice to take two cases. In the first case chemical reactions are accounted for in an apparent activation energy and a pre-exponential factor. In the second case heat transfer is accounted for by thermal conductivity.

4.1 Model Formulation

A mathematical model is developed to attempt to describe the physical and chemical processes which occur during pyrolysis. The model is considered to be a one dimensional heat transfer through the radial direction of a cylindrical rice hull pyrolysis unit. Figure 4.1 shows various heat transfer processes which will be included in this model. Q_1 is the heat source with heat transfer to rice hull from cylindrical furnace wall. Q_2 is the heat conduction in the rice hull bulk and Q_3 is the net heat of reactions due to pyrolysis.

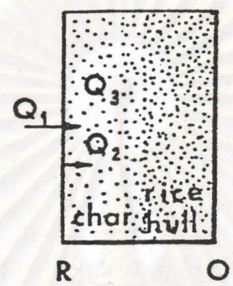

Figure 4.1 Schematic Diagram of the Heat Transfer Model

The present one-dimensional model has included several assumptions. They are :

1. Heat transfer within the rice hull bed is only by conduction,

2. The pore structure allows the volatiles to leave the solid matrix as soon as they are formed, without any thermal interaction,

3. The heat loss due to volatile outflow is negligible,

4. The heat constant is constant,

5. The pyrolysis reaction is represented by a single reaction of the first order of the Arrhenius type (as suggested by Bamford et al).

$$S \longrightarrow a\,V \quad + \quad b\,C \qquad (4.1)$$

(solid reactant) (fluid product) (solid product)

The partial differential equation is obtained from the energy balance over a cylindrical shell of thickness Δr and length L as follows :

$$q_r 2\pi r L\Big|_{r+\Delta r} - q_r 2\pi r L\Big|_r - 2\pi r \Delta r L Q\left(-\frac{\partial \rho}{\partial t}\right) = 2\pi r \Delta r L \frac{\partial(\rho C_p T)}{\partial t} \qquad (4.2)$$

with

$$q_r = -k\frac{\partial T}{\partial r} \qquad (4.3)$$

Dividing by $2\pi\Delta r L$ and taking the limit as Δr approach zero gives

$$\frac{\partial(\rho C_p T)}{\partial t} = \frac{1}{r}\frac{\partial(q_r r)}{\partial r} + Q\left(\frac{\partial \rho}{\partial t}\right) \qquad (4.4)$$

The term in the left hand side of equation (4.4) accounts for the change in the sensible heat, while the first term of the right hand side accounts for the conduction heat transfer through the solid. The last term of the right hand side accounts for the net heat of reaction within the solid.

The kinetics on the pyrolysis reactions represents the rate of weight loss per unit volume which is a global first order Arrhenius reaction (n=1) as follows :

$$-\frac{\partial \rho}{\partial t} = A\exp\left(-\frac{E}{R_g T}\right)(\rho - \rho_\infty) \qquad (4.5)$$

4.2 Initial and Boundary Conditions

For a cylindrical sample, the initial and boundary conditions are given as follows :

At $t = 0,\ 0 \leqslant r \leqslant R$

$$T = T_o, \quad \rho = \rho_o \qquad (4.6)$$

At $t > 0,\ r = R$ (furnace wall)

$T = T_w$ (being the wall temperature, measured using a thermocouple) (4.7)

At $t > 0,\ r = 0$ (central axis of the rice hull bed)

$$\left.\frac{\partial T}{\partial r}\right|_{r=0} = 0, \quad \left.\frac{\partial \rho}{\partial r}\right|_{r=0} = 0 \qquad (4.8)$$

4.3 Evaluation of Equation Parameters

In the energy equation(4.4), there are four parameters that account for the pyrolysis process consist of heat capacity, heat of reaction, kinetic parameters, and thermal conductivity.

Heat capacity is one parameter that will affect the model prediction. As there was no available data published in the literature, the heat capacity of rice hull used in equation (4.4) was determined by undertaking experiment at various conditions.

During pyrolysis, chemical reactions occur in the solid as result in change enthalpy represent in heat of reaction. Heat of reactions in the mathematical model is divided into two ranges. In the first range at a local temperature below 200 °C, the heat of reaction is assumed to equal the heat of evaporation. In the second range at a local temperature above 200 °C, the heat of reaction is read from Figure 4.2.

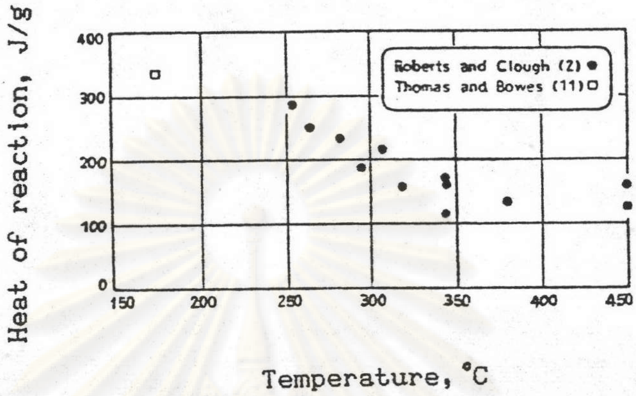

Figure 4.2 Experimentally Determined Values of Heat of Reaction Plotted Against a Temperature (Roberts, 1971)

The kinetic parameters obtain from using the kinetic model fits the experimental data which represents in activation energy and pre-exponential factor values.

The last parameter in the mathematical model is the thermal conductivity and one of the major parameters that affects the pyrolysis system. The thermal conductivity is determined by using the mathematical model to fit the experimental temperature profiles.