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# Optimisation of Operating Parameters in Multi-Stage Pyrolysis

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Pyrolysis process is considered as a beneficial option in waste treatment largely due to the products generated and the energy recovery when compared to other methods. In the conventional pyrolysis process, heat is continually supplied to the reactor until the final pyrolysis temperature is attained. The reactor is then maintained isothermally at this temperature until the pyrolysis is completed. This technique does not take into consideration the mechanism of the pyrolysis which involves both exothermic and endothermic reaction and the opportunity of gaining some processing benefits is often ignored. Multi-stage pyrolysis which is an approach to carry out pyrolysis with multiple heating stages in order to gain certain processing benefits has been introduced in our earlier works. 22.5 % energy reduction was achieved in our past work with a 100 % increase in completion time. This work therefore proposes the optimisation of the operating parameters in multi-stage pyrolysis in order to limit the increase in completion time and also reduce the overall energy. This approach can achieve a 29 % reduction in energy usage with just 36 % increase in completion time.

## 1. Introduction

Pyrolysis process is considered as a beneficial option in waste treatment largely due to the products generated and the energy recovery when compared to other methods, though the economical issues is still a concern due to the amount of energy used for pyrolysis (Senneca et al., 2001).

Pyrolysis process is majorly overall endothermic though it involves series of both exothermic and endothermic processes (Sharma et al., 1998; Yang and Roy, 1996). During the pyrolysis process, organic matters are cracked down into smaller fraction and results in the given out of energy (exothermic reactions) and as the temperature progresses, secondary products are formed as well as volatile during the vaporisation reaction (endothermic reaction). Since the pyrolysis of waste tyre is overall endothermic therefore there is net energy input required for the process.

The conventional pyrolysis process does not take into consideration the opportunity to gain certain processing benefits during the heating of the reactor and excess amount of heat are applied into the process. This contributed to the limitation of pyrolysis as an energy intensive process.

Multi-stage pyrolysis has been introduced in earlier work (Cheung et al., 2011). This is an operation strategy to carry out pyrolysis with multiple heating stages in order to gain certain processing benefits. We proposed four stages of heating – adiabatic – heating – adiabatic. The feasibility of the multi-stage process as a method of reducing the overall energy usage in pyrolysis has been demonstrated in the previous work and we reported that the process can reduce the overall energy usage in the pyrolysis by 22.5 % though with 100 % increase in completion time (Cheung et al., 2011).

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Previously only time duration was used as the basis for switching between the different stages and also same heating rate was applied for the two heating stages.

In multi-stage pyrolysis, the temperatures to switch to the different stages are very important and can determine the final overall heat requirement and the completion time. If the first adiabatic temperature stage is too low (< 250 $^{o}$C), cracking may not be initialise on time therefore takes a lot of time and if the first adiabatic temperature is too high (> 400 $^{o}$C), the exothermic heat may not have been fully used up therefore there is need to optimise the temperature to switch to the first adiabatic as well as the time duration at this stage. Heating rate for the different heating stage is another important consideration that can affect the efficiency of the multi-stage pyrolysis since waste tyre exhibits different kinetics behaviours at different heating rate (Quek and Balasubramanian, 2009). Heating rate can affect the amount of energy applied to the pyrolysis as well as the pyrolysis completion time. In this work, the possibility of using a lower or higher heating rate for the second heating stage was explored and based on the experimental heat flow plot for the waste tyre, the behaviour of the different heating rate after 300 $^{o}$C is independent of the initial starting heating rate.

The objective of this work is to optimise the operating parameters in multi-stage pyrolysis to reduce the overall energy usage and limit the increase in completion time. Optimisation techniques was applied to determine the best strategy to use by selecting the best temperature and time duration of each stage in order to have good process efficiency and to reduce the overall energy used while maintaining the completion time within a set limit. The use of different heating rates for the second heating stage was also considered and different optimisation methods were used. The success of this work is expected to make multi-stage pyrolysis a new consideration for pyrolysis technique and thereby improving the economic advantages of pyrolysis process.

## 2. Methodology

The experimental results obtained from the thermogravimetric and differential thermal analysis were used to obtain the pyrolysis kinetics and the heat flow parameters. The parameters were then used to build a tyre pyrolysis model to describe the mass loss and the heat transfer phenomena of the tyre pyrolysis. In developing the model, it was assumed that the pyrolyzing tyre particle is spherical, the mode of heat transfer within the particle is by conduction only and the volatiles produced during the pyrolysis are assumed to leave the pyrolysis environment immediately.

### 2.1 Experimental

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques were performed on the cotton tyre samples using the machine TGA/DTA 92 Setaram II to study the pyrolysis kinetics. The samples were heated from ambient temperature to 600 $^{o}$C with nitrogen gas used as the carrier gas at fixed flowrate (16.7 mL/min) and different heating of 2, 5, 10 and 20 $^{o}$C/min. were used and the obtained kinetics and heat flow parameters were employed to build the pyrolysis model. Figure 1 shows the heat flow plot at different heating rates.

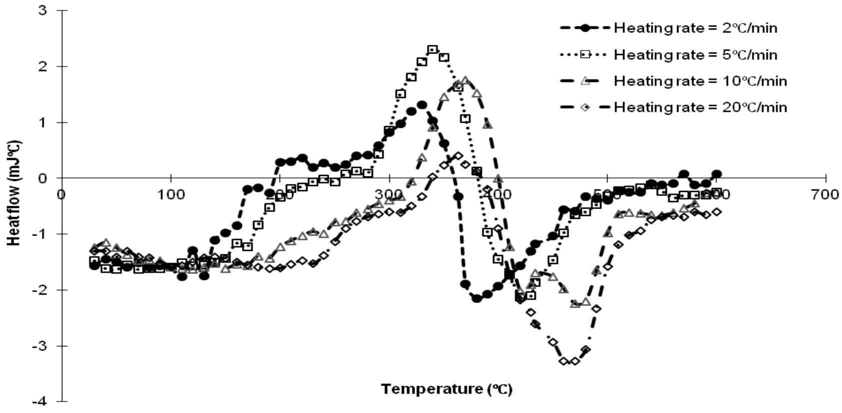

*Figure 1: Heat flow of 10mg waste tyre under different heating rate*

## 2.2 Modelling of the tyre pyrolysis

The details of the kinetics framework were explained extensively in previous works (Cheung et al., 2011), it is based on the tyre pyrolysis mechanism by Senneca et al (Senneca et al., 2001). The mechanism as illustrated in Figure 2 consists of three mass loss equations (R1, R3a and R3c) which are majorly endothermic reactions and two exothermic reactions (R2 and R3b) which contributes to the exothermic peaks in the DTA plot.

In previous work, the heating trend of the pyrolysis progress was modelled to be static i.e. the heat of reactions in every parts are governed by the bulk heating rate rather than the local heating rates. This work uses the dynamic heating approached which makes the heat of reactions and the kinetics governed by the local heating rates at each layer of the pyrolysis. The mass loss and the heat flow kinetics are summarised below, the kinetics parameters and detailed explanation are given in another work (Lam et al., 2011).

| | | | | |
|---|---|---|---|---|
| R1 | Tyre additives | → | Volatiles | + Char |
| R2 | Tyre rubbers | → | Intermediate A | |
| R3a | Intermediate A | → | Volatiles | + Char |
| R3b | Intermediate A | → | Intermediate B | |
| R3c | Intermediate B | → | Volatiles | + Char |

*Figure 2: Waste tyre pyrolysis mechanism*

The pyrolysis kinetic is governed by:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i} \qquad (1)$$

$$\frac{d\gamma_i}{dt} = A_j \exp\left(-\frac{E_j}{RT}\right)(1-\gamma_j)^{n_j} \qquad (2)$$

$$\alpha_T = \sum_i \omega_i \alpha_i \qquad (3)$$

$$\omega_i = a_i \beta^2 + b_i \beta + c_i \qquad (4)$$

The heat flow kinetics is given as;

$$q_r = -4\pi^2 \lambda \frac{\partial T}{\partial r} \qquad (5)$$

$$q_{r+\square r} = q_r + \frac{\partial q_r}{\partial r} \Delta r \qquad (6)$$

The overall heat of mass loss reactions is given by

$$q_{mlr} = 4\pi r^2 \rho \Delta r \sum_i \left( H_i \frac{\partial \alpha_i}{\partial t} w_i \right) \qquad (7)$$

and, the overall heat of exothermic reactions is given by

$$q_{exo} = 4\pi r^2 \rho \Delta r \sum_j \left( H_j \frac{\partial \gamma_i}{\partial t} \right) \qquad (8)$$

The sensible heat ($q_s$) in each layer is

$$q_s = 4\pi r^2 \rho \Delta r\, C_p \frac{\partial T}{\partial t} \qquad (9)$$

The overall heat balance in the layer with radius *r* is

$$q_s = q_r - q_{r+\Delta r} + q_{mlr} + q_{exo} \qquad (10)$$

The energy conservation equation is therefore expressed as;

$$\frac{\partial T}{\partial t}=\frac{\lambda}{\rho C_p}\frac{\partial^2 T}{\partial t^2}+\frac{2}{r}\frac{\lambda}{\rho C_p}\frac{\partial T}{\partial r}+\frac{1}{C_p}\sum_i\left(H_i\frac{\partial \alpha_i}{\partial t}\omega_i\right)+\frac{1}{C_p}\sum_j\left(H_j\frac{\partial \gamma_j}{\partial t}\right) \tag{11}$$

The variation of the heat capacity, the thermal conductivity, the heats of mass loss reaction and the heats of exothermic reaction are given by

$$\lambda=\frac{(\alpha_{T,f}-\alpha_T)}{(1-\alpha_{T,f})}\lambda_{tyre}+\frac{\alpha_{T,f}}{(1-\alpha_{T,f})}\lambda_{carbon} \tag{12}$$

$$\lambda=\frac{(\alpha_{T,f}-\alpha_T)}{(1-\alpha_{T,f})}\lambda_{tyre}+\frac{\alpha_{T,f}}{(1-\alpha_{T,f})}\lambda_{carbon} \tag{13}$$

$$H_i=a_{H,i}\beta^2+b_{H,i}\beta+c_{H,i} \tag{14}$$

$$H_j=a_{H,j}\beta^2+b_{H,j}\beta+c_{H,j} \tag{15}$$

Imposing the boundary conditions,

B.C. 1: $-\lambda\frac{\partial T}{\partial r}=h(T_R-T_{bulk})$ (16)

B.C. 2: $\frac{\partial T}{\partial r}\Big|_{r=0}=0$ (17)

## 3. Multi-stage Pyrolysis

In the previous work on multi-stage pyrolysis, it was stated that multi-stage pyrolysis can help to reduce energy consumption by 22.5 % but the completion time increased by 100 % in the process. Reduction in energy consumed during pyrolysis is worthwhile but not so much at the expense of the completion time. The efficiency of a pyrolysis process is also determined by the processing time. The concept of multi-stage is to take advantage of the thermal behaviour of pyrolysis and reduce the excess amount of heat into the process by carrying out the process in several stages. Four stages were proposed i.e. Heating – Adiabatic – Heating – Adiabatic.

Three parameters are very important which subsequently drive the amount of energy reduced and the extent of the increase in completion time. They are; target temperature to switch to the first adiabatic, the time duration in the first adiabatic stage and the temperature to switch to the second adiabatic stage. Since there are various possibilities and combinations, we decided to use an optimisation technique to determine an optimum point for these parameters. A detailed study of the DTA plot in Figure 1 suggested that heat supplied to the pyrolysis reaction is used to initialise the exothermic reaction at the early stage and the endothermic reaction only starts above 350 $^{o}$C for lower heating rates, therefore the capture heat during the first heating stage can be used for the pyrolysis under the adiabatic stage. The process is more exothermic at temperature between 250 – 380 $^{o}$C which shows that more heat is generated and used up in the endothermic reaction between 380 – 500 $^{o}$C. We therefore propose efforts to both reduce the energy consumed and a limit to the increased in completion time.

## 4. Optimisation study

Optimization model was developed to utilize the kinetic model in a way to reduce the energy used subject to several constraints. The waste tyre pyrolysis model is a non-smooth function with boundary constraints therefore the overall energy was set as the objective function while limiting the completion time. A limit of 40 % increase in completion time was set as a constraint and from our work on optimisation of particle size (Oyedun et al., 2012), we chose 35 mm as the desired particle size. Since the completion time for the conventional pyrolysis was 1.47 h.

$$\begin{aligned} &\min E_T \\ s.t.\quad & t_{complete} \le 2.06\, h \\ & 250 \le T_{adia1} \le 350 \\ & 5 \le t_{adia1} \le 30 \\ & 450 \le T_{adia2} \le 510 \end{aligned} \tag{18}$$

Where $E_T$ is the overall heat requirement (J/g-tyre), $t_{complete}$ is the completion time (h), $T_{adia1}$ is the temperature to switch to first adiabatic stage ($^oC$), $t_{adia1}$ is the time duration for the first adiabatic stage and $T_{adia2}$ is the temperature to switch to the second adiabatic stage ($^oC$). The heating rate of $10^oC$/min ($h_{r1}$) was used for the two heating stages for the first case scenario but when considering the second case scenario, a constraint was added to vary the heating rate for the second heating stage as;

$$2 \le h_{r2} \le 20 \tag{19}$$

Where $h_{r2}$ is the heating rate for the second heating stage ($^oC$/min).

The optimisation toolbox in MATLAB was used and different solvers including fmincon, pattern search and simulannealbnd solvers were used. Based on the nature of the objective function, it takes so much time and 4000 iterations to find the global optimum and the simulannealbnd provided the best results.

## 5. Results and discussion

The optimisation model was run using the pyrolysis model and the results were analysed based on the scenarios of using same heating rate or different heating rate for the second stage.

*Table 1: Overall heat requirement and completion time for the two case scenarios*

| Approach | Overall heat requirement (J/g-tyre) | Completion time (h) |
|---|---|---|
| Conventional | 673.74 | 1.47 |
| Multi-stage (Case 1) | 484.69 | 2.02 |
| Multi-stage (Case 2) | 457.74 | 2.00 |

### 5.1 Case 1: Same Heating rate

The result of the overall heat requirement for this case is presented in Table 1. The overall heat requirement decreased by 24.7 % while the completion time increased by just 37 %. Table 2 present the optimisation result of this case scenario. The reactor temperature was raised from 30 $^oC$ to 309 $^oC$ at heating rate of 10 $^oC$/min for the first heating stage. The process then switches to the adiabatic mode for 15 min. During this time, processing benefits can be gained from the process and all available excess heat in the process was used up to facilitate the pyrolysis process. The heating resumes after 15 min and raised the temperature to 491 $^oC$ for the second heating stage. After the second heating stage, adiabatic process steps in and the remaining excess heat was used to complete the pyrolysis process. The temperature profile for this case is illustrated in Figure 3.

*Table 2: Optimisation result for the same heating rate approach*

| $h_{r1}$ ($^oC$/min) | $h_{r2}$ ($^oC$/min) | $T_{adia1}$ ($^oC$) | $t_{adia1}$ (min) | $T_{adia2}$ ($^oC$) |
|---|---|---|---|---|
| 10 | 10 | 309 | 15 | 491 |

### 5.2 Case 2: Different Heating rate

The concept of second heating rate was introduced in this work. Multi-stage pyrolysis consists of more than one heating stage. The result for this case is presented in Table 3, it shows that the overall heat decreased by 29 % while the completion time increased by 36 %. This result is better than that obtained in case 1. The optimisation result in Table 3 indicated that while 10 $^oC$/min was used for the first heating stage, there was a switch to 5 $^{o}$C/min for the second heating stage. This result can be justified from the DTA plot in Figure 1. The endothermic peaks for the lower heating rates are lower than that of the higher heating rates and therefore less heat are used overall by the lower heating rate for the second heating stage. The result shows that the first adiabatic starts at a temperature of 280 $^{o}$C lower than that of the case 1 but the time duration was few seconds longer than that of case 1. Also, the temperature for the second adiabatic temperature is 481 $^{o}$C.

*Table 3: Optimisation result for the different heating rate approach*

| $h_{r1}$ ($^{o}$C/min) | $h_{r2}$ ($^{o}$C/min) | $T_{adia1}$ ($^{o}$C) | $t_{adia1}$ (min) | $T_{adia2}$ ($^{o}$C) |
|---|---|---|---|---|
| 10 | 5 | 280 | 15.13 | 481 |

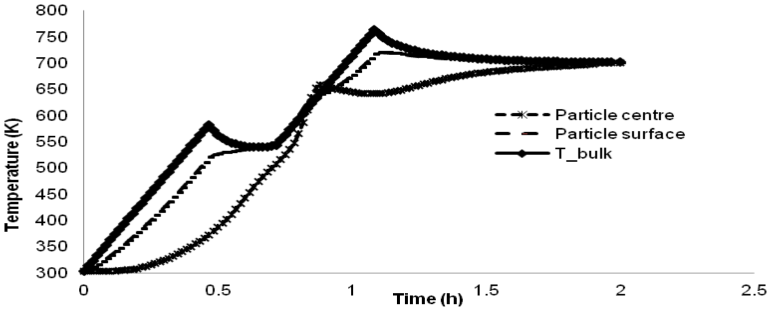

*Figure 3: Temperature profile for the multi-stage pyrolysis (case 1)*

## 6. Conclusion

Multi-stage pyrolysis process can be used to obtain certain processing benefits during pyrolysis process. Optimisation technique can be used to optimise the operating parameters so as to reduce the overall heat required for the process. The completion time is also very important consideration and its increase must be limited if the process will be efficient. In this work, we modified the multi-stage pyrolysis model in earlier work and include an optimisation model. The optimised multi-stage pyrolysis approach can reduce the energy usage by 29% while increasing the completion time by 36 % which is far better compared to the earlier result.

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