Multi-stage Waste Tyre Pyrolysis: An Optimisation Approach

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Extensive studies on pyrolysis as a way to convert waste organic materials into useful products have been carried out for decades. In waste tyre pyrolysis, the products yielded are suitable for use as fuel. But on the other hand, the process is energy intensive. This work therefore proposes a multi-stage design to optimize a waste tyre pyrolysis process by minimizing the energy usage. The degradation kinetics and the heat flow of tyre in pyrolysis were first studied by thermal analysis. The results were used to construct a tyre particle pyrolysis model for verifying the proposed multi-stage pyrolysis approach. It was shown by the model that the proposed multi-stage tyre pyrolysis design can reduce energy usage by 21.7 %. This approach for optimizing the waste tyre pyrolysis through the thermal studies on tyre and the multi-stage design is believed to be applicable to other feedstock such as waste biomass.

1. Introduction

As automobiles have become a vital part of today's society, the disposal of waste tyres has become a major, worldwide environmental issue. Each year, 5 Mt of tyres are scrapped (Singh et al., 2009). Currently there are research being undertaken to study the use of pyrolysis as an energy and material recovery process for waste tyres. Pyrolysis is the thermal decomposition of organic materials at elevated temperatures in the absence of oxygen. It yields carbonaceous residues, liquid hydrocarbons and combustible gases. In waste tyre pyrolysis, the non-condensable gases, pyrolysis oil and tyre char generated have properties suitable for use as a fuel substituent.

Pyrolysis consists of exothermic primary cracking reactions, endothermic secondary cracking reactions and vaporization process. The endothermic processes dominate the energy requirement of pyrolysis process and therefore, most of the pyrolysis processes are globally endothermic (Sharma et al., 2000). Conventional approaches of pyrolysis do not take into account the thermal behaviour of pyrolysis and applies excess amount of heat into the process for the completion of pyrolysis. Because of the energy intensive nature of pyrolysis, it limits the prospect of using pyrolysis for making fuel substituent. Using waste tyre as the subject of study, this paper therefore proposes a multi-stage pyrolysis as an approach to optimize waste tyre pyrolysis process by minimizing the pyrolysis energy requirement.

Please cite this article as: Lam K. L., Lee C. W. and Hui C. W., (2010), Multi-stage waste tyre pyrolysis: An optimisation approach, Chemical Engineering Transactions, 21, 853-858 DOI: 10.3303/CET1021143

2. Paper approach

The approach for this work was to first model the experimental results from the thermogravimetric analysis and differential thermal analysis to obtain tyre pyrolysis kinetics parameters and heat transfer parameters. The parameters were then used to build a tyre particle pyrolysis model that describes the mass loss and heat transfer phenomena of single tyre particle pyrolysis. The model was used as the basis for making comparison between conventional pyrolysis approach and the proposed multi-stage pyrolysis approach.

2.1 Experimental work

Thermal analysis (Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)) were performed on waste tyre samples using TGA/DTA 92 SETARAM II with a nitrogen atmosphere at different heating rates 2, 5, 10 and 20 $^{\circ}$ C /min.

2.2 Modeling of tyre pyrolysis kinetics and heat flow

A mathematical model is used to describe the mass loss kinetics and heat flow of tyre pyrolysis. The tyre pyrolysis mechanism is based on three major reaction paths (Senneca et al., 1999).

Reaction path 1:	Organic tyre additives -> Volatiles + Char
Reaction path 2:	Rubber -> Intermediate A
Reaction path 3a:	Intermediate A -> Volatiles + Char
3b:	Intermediate A -> Intermediate B
3c:	Intermediate B -> Volatiles + Char

The model composes of endothermic mass loss kinetics and exothermic cracking kinetics. In this proposed mechanism, reactions 1, 3a and 3c are the mass loss reactions that contribute to endothermic heat. The mass loss kinetics is described by:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(\frac{-Ea_i}{RT}\right) (1 - \alpha_i)^{\eta_i} \tag{1}$$

where a_i represents the mass loss conversion of reaction *i*, *t* is the time, A_i is the preexponential factor of reaction *i*, Ea_i is the activation energy of reaction *i*, *R* is the universal gas constant, *T* is the absolute temperature and n_i is the reaction order of reaction *i*. TGA results were used to determine the mass loss kinetics parameters in Eq.1. The cracking reaction kinetics is given by:

$$\frac{d\gamma_j}{dt} = Ac_j \exp\left(\frac{-Ec_j}{RT}\right) (1 - \gamma_j)^{\eta_j}$$
(2)

where γ_j is the conversion of exothermic reaction *j*, Ac_j is the pre-exponential factor of reaction *j*, Ec_j is the activation energy of reaction *j* and n_{cj} is the reaction order of reaction *j*. DTA results were used to determine the kinetics parameters for Eq.2. Heat of vaporization (hg_i) and exothermic reaction heat (hc_j) were determined from equations 1 and 2 by a baseline method (Yang and Roy, 1999). Because of the good fitting between the model and the experimental data, it can be concluded that the proposed reaction framework is a good representation of tyre pyrolysis and was used for building the tyre particle pyrolysis model.

2.3 Tyre particle pyrolysis model

Using the kinetics and heat transfer parameters from the modeling results, a single tyre particle pryolysis model was constructed. In the model, it is assumed that the tyre particle is spherical and is heated up by pyrolysis gas by convection inside the reactor while heat is transferred inside the particle by conduction only. In the reactor, the reactor temperature is assumed to be the same as the pyrolysis gas temperature. Based on the terms listed in Table 1, the heat balance can be described in terms of the particle temperature change across the radius and time by Eq. 3.

Table 1: Heat balance terms in the layer with radius r

Heat conducted into the layer with radius r, q_r	$-4\pi r^2 \cdot \lambda \cdot \frac{\partial T}{\partial r}$	
Heat conducted out of the layer with radius r, q_{r+dr}	$q_r + \frac{\partial q_r}{\partial r} \cdot \Delta r$	
Endothermic heat, q_{end}	$\sum_{i} \left(hg_i \cdot \frac{\partial \alpha_i}{\partial t} \cdot \omega_i \right) \cdot 4\pi r^2 \cdot \rho \cdot \Delta r$	
Exothermic heat, q_{exo}	$\sum_{j} \left(hc_{j} \cdot \frac{\partial \gamma_{j}}{\partial t} \right) \cdot 4\pi r^{2} \cdot \rho \cdot \Delta r$	
$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho C p} \cdot \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \cdot \frac{\lambda}{\rho C p} \cdot \frac{\partial T}{\partial r} + \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) - \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot \frac{\partial \gamma_j}{\partial t} \right) = \frac{1}{C p} \cdot \sum_j \left(hc_j \cdot$	$\sum_{i} \left(hg_i \cdot \frac{\partial \alpha_i}{\partial t} \cdot \omega_i \right) \tag{3}$	

where λ is the particle thermal conductivity, Cp is the heat capacity, ρ is the density of tyre particle and is assumed to be constant, r is the radius of the layer, hg_i is the heat of vaporization, hc_j is the exothermic reaction heat and ω_i is the coefficient of mass loss contribution due to reaction *i*. Explicit finite difference method was used to solve Eq. 3.

2.4 Multi-stage pyrolysis

With an insight of the thermal behaviour of waste tyre from the TGA, DTA result and the tyre particle pyrolysis model, a multi-stage pyrolysis approach is therefore proposed to enhance a waste tyre pyrolysis process. The approach is to incorporate our understanding of the thermal behaviour of the waste tyre into the pyrolysis process design by dividing a pyrolysis process into several heating stages, so as to reduce the overall process heat requirement and to provide a better control of products' yield and quality. While there can be different ways of implementing the multi-stage pyrolysis approach, one of them is demonstrated in this paper to target on minimizing process heat in waste tyre pyrolysis.

For a large tyre particle in the magnitude of centimetre, there exists significant heat transfer barrier within the particle due to its poor thermal conductivity. Thus, the pyrolysis profile on the particle surface is faster than that of the inner part. It is known from the thermal analysis that in pyrolysis, an exothermic stage occurs before the endothermic stage. It provides an opportunity to utilize the exothermic heat if it is captured inside the system to facilitate the endothermic heat consumption afterwards. In addition, pyrolysis, some heat is used to heat up the pyrolysed part of the particle. In this work, adiabatic stages are thus added for better energy utilization.

3. Case Study

3.1 Scenario

The tyre particle pyrolysis model was used to evaluate on the pyrolysis performance of conventional approach and multi-stage approach, as shown in Table 2. It is assumed in this study that pyrolysis is performed on tyre particle with radius of 3 cm in a batch reactor that can provide a constant heating rate environment. Heating rate of 10 °C/min and target pyrolysis temperature of 510 °C were used as the basis for both approaches.

Table 2: Pyrolysis approach used in case studies

Conventional pyrolysis approach			approa	ch	Multi-stage pyrolysis approach	
Single stage with a constant heating rate		eating rate	1st stage: constant heating rate			
until	reaching	the	target	pyrolysis	2nd stage: adiabatic	
temperature					3rd stage: constant heating rate	
					4th stage: adiabatic	

3.2 Conventional pyrolysis approach

A single stage pyrolysis is used as the conventional approach. The reactor temperature is raised from 30 °C to 510 °C with a constant heating rate of 10 °C/min and afterwards, the temperature is kept constant at 510 °C. The model calculated that the tyre particle completes pyrolysis in about 1.19 h and required 643.77 J/g tyre of energy. Figure 1(a) shows the mass loss fraction profile of a tyre particle during pyrolysis. When the mass loss fraction reaches the maximum pyrolysable fraction for tyre of 0.55, the pyrolysis in that layer is completed. The particle surface finishes pyrolysis faster than the interior part because of the heat transfer barrier, as shown in Figure 1(b) that the particle surface temperature is higher than the particle centre temperature during the majority part of the pyrolysis period. It is also noted that the heat applied drop to low levels after the two peaks. Two adiabatic stages are thus used for the regions with low heat applied.



Figure 1: Modeled result in conventional approach (a) Mass loss fraction profile (b) Temperature profile and Heat applied profile

3.3 Multi-stage pyrolysis approach

3.3.1 First adiabatic stage

The heat applied profile, in Figure 1(b), gives the hint for the possible time of having the first adiabatic stage. It can be observed that after 0.4 h, the heat applied begins to drop. It indicates that the exothermic heat is getting dominated, first at the particle

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surface and later progress to the particle core. An adiabatic period of 0.25 h, which is approximate the duration between the first peak and the first trough, was chosen. The onset time for this adiabatic stage was selected to be at 0.47 h as it gives the minimum overall process energy requirement, as shown by the arrow in Figure 2(a).



Figure 2: (a) Heat applied and overall heat requirement in the selected region (b) Mass loss fraction profile after adding the first adiabatic stage

3.3.2 Second adiabatic stage

Heating resumes after the first adiabatic stage as the heat applied before the first adiabatic stage is not enough to complete the pyrolysis. It can be noted from Figure 2(b) that at time 1.15 h (shown by the arrow), the pyrolysis on the particle surface has completed. However, heat is still being applied to the particle to raise the temperature further instead of facilitating the pyrolysis. Therefore, in addition to the first adiabatic stage, a second adiabatic stage was added after 1.15 h to reduce the energy consumption by allowing the sensible heat within the particle to drive the pyrolysis to completion. The selection of the onset time for the second adiabatic stage is a tradeoff between the overall heat requirement and the completion time, as shown in Figure 3(a). The onset time was selected to be at 1.2 h (vertical line) for a balance between the finishing time and the energy usage. Figure 3(b) summarizes the result.



Figure 3 (a) Overall heat requirement and completion time at different onset time for second adiabatic stage (b) Particle centre mass loss fraction profile and reactor temperature for multi-stage and conventional approach

3.4 Results and discussion

As shown in Table 3, despite of the doubling of the processing time, the multi-stage approach can save about 21.7 % of energy compared to the conventional approach.

Table 3 Overall heat requirement and processing time for the two approaches

Approach	Overall heat requirement (J/g·tyre)	Processing time (h)
Conventional	643.77	1.19
Multi-stage	503.91	2.37

This case study gives a demonstration on how our thermal and kinetics understanding on tyre together with multi-stage pyrolysis can be used to optimize the energy usage in waste tyre pyrolysis. The heat requirement at different time of the pyrolysis profile is different. Instead of an uniform global pyrolysis condition in the conventional approach, a multi-stage approach utilizes several stages with different pyrolysis condition to provide a better control of energy usage. By taking into account the other pyrolysis conditions, such as heating rate, vapour residence time and reactor configuration, the model will be more descriptive. The approach will not only provide energy optimization, but also can be used to optimize the throughput of the products. In addition, the approach used in this work is not restricted to waste tyre pyrolysis, it is believed to be also applicable for waste biomass pyrolysis.

4. Conclusions

Pyrolysis is a method to recover material and energy from waste tyre. Because of its energy intensive nature, it is critical to optimize the process by minimizing the energy usage. In this work, thermal analysis was used to study the kinetics and heat flow of tyre pyrolysis. The modeled result was used to build a tyre particle pyrolysis model to compare between the conventional pyrolysis and the proposed multi-stage pyrolysis. The multi-stage pryolysis approach can reduce the energy usage by 21.7 %.

Acknowledgement

The authors gratefully acknowledge the support from Hong Kong RGC research grant (No. 613808, 614307) and Global Power and Energy Company Limited.

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