

THERMOLYSIS AND KINETICS OF SCRAP TYRE AND BAGASSE FOR ENERGY UTILIZATION

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ABSTRACT

The increase of energy demand has brought concern to find alternative fuel that will at least sustain the requirement. Bagasse and scrap tyre are waste generated in our industrial activities, which can be used in energy production to subsidize the demand. This paper, aim to study the decomposition behaviour and kinetics of biomass (bagasse) and scrap tyre as preliminary stage of fuel sample analysis to be considered for energy production in gasification/combustion or pyrolysis facilities. The behaviour demonstrated with thermogravimetric analyzer (TGA), shows that all samples have high volatile amount release, 84.21% for bagasse and 85.08% for scrap tyre, which means all are suitable for pyrolysis. However, scrap tyre is most suitable for gasification or combustion due to its high energy content, high ash content and low moisture than bagasse. The determined kinetic parameter were activation energy (E) and pre-exponential factor (A) for hemicellulose/oil as first release composite and cellulose/elastomer as second composite of the analyzed bagasse/scrap tyre samples. The hemicelluloses of bagasse exhibited highest value of activation energy and pre-exponential factor ($E=178.191$ kJ/mol, and $A=1.74 \times 10^{16}$) than oil of scrap tyre ($E=41.113$ kJ/mol, and $A= 495.5$), which means bagasse is suitable candidate for gasification process due to high operating temperature. With this respect of the study, all candidates may be suitable for pyrolysis or gasification/combustion process. However, for environmental consideration scrap tyre is not suitable due to high sulphur (S) and nitrogen (N) content resulting to high emission of SO_x and NO_x .

Keyword: Bagasse, Scrap Tyre, TGA, Kinetics, Peak properties

INTRODUCTION

Energy is necessary for daily survival. Future development crucially depends on its long-term availability in increasing quantities from sources that are dependable, safe, and environmentally sound (Kohli *et. al*, 1996). At present, no single source or mix of sources is at hand to meet this future need. Today's primary sources of energy are mainly non-renewable: natural gas, oil, coal, peat, and conventional nuclear power. There are also renewable sources, including wood, plants, dung, falling water, geothermal sources, solar, tidal, wind, and wave energy. In theory, all the various energy sources can contribute to the future energy mix worldwide. However, each has its own economic, health, and

environmental costs, benefits, and risks factors that interact strongly with other governmental and global priorities. Choices must be made, but it is common knowledge that choosing an energy strategy inevitably means choosing an environmental strategy.

The growth of energy demand in response to industrialization, urbanization, and societal affluence had led to extremely uneven global primary energy consumption. Many forecasts of recoverable oil reserves and resources suggest that oil production will level off by the early decades of 21st century and then gradually fall during a period of reduced supplies and higher prices (Victor, 2008).

The appetite for oil and other energy sources is growing dramatically, with worldwide energy consumption projected to increase by 36% by 2035 (Energy supply & demand, 2011). The growing demand is fuelled by increase in population, with most of that growth in countries with emerging economies, such as China and India. Rising energy demand from economic output and improved standards of living will likely put added pressure on energy supplies.

In international public opinion surveys there is strong support for promoting alternative energy sources. The term 'alternative energy' implies energy that is used as an alternative to using fossil fuels. These energy sources can be easily used to turn turbines in a generation process and thus replace oil and natural gas. However, once the technology is perfected, these sources will prove to be the most cost effective (Importance of Alternative Energy, 2012).

In this paper scrap tyre and biomass (bagasse) waste are analyzed for fuel suitability in thermal conversion systems. The elemental analyzer, auto-bomb calorimeter and thermo-gravimetric analyzer, have been useful in thermal analysis of materials (Daniel *et. al.*, 1991; Mu, 1982).

During thermal degradation of decomposing material, the contained components are likely to react independently. However, most of the studies simplify and lump as a single reactant (Tsamba, 2008). The kinetic study takes into account the decomposition rate to describe the properties of individual contained components.

A primary and relatively new way to utilize waste to recover energy, represent an attractive alternative to other fuels and in environmental management. On average, the energy content of tyre range between 27-29 MJ/kg and biomass 15-23

MJ/kg; the values vary because of the varying composition of each fuel (Giere *et. al.*, 2004; Ciolkosz *et. al.*, 2010).

METHODOLOGY

1 Materials and Experiment

Tyre sample were processed in two physical processing steps: chipping/shredding and metal removal and thereafter ground to smaller particle sizes of about 1 ± 0.5 mm diameter for experiments. Also bagasse was ground and sieved to 1 ± 0.5 mm particle size for characterization purpose for each experiment. The ground samples were stored in a plastic bag in order to prevent contact with air moisture.

Standard test methods for proximate, elemental analysis and higher heating values (HHV) were done. This is important since the heating value of sample is highly correlated with the content of ash, volatiles, including the elemental composition of carbon, hydrogen, and oxygen for validation of fuel in energy application (Jenkins, 1985).

The HHV was measured experimentally, the standard method uses auto-bomb calorimeter device. The device burns a small sample mass of 10 ± 0.2 mg in the presence of oxygen inside a sealed container (or bomb). The heat released from combustion is transferred to the fluid (water) that surrounds the container. The heating value was calculated from the product of net temperature increase and specific heat of fluid per mass of sample.

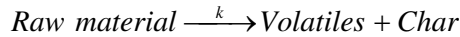
Thermogravimetric test were performed with analyzer type NETZSCH STA 409 PC Luxx to investigate the thermal behavior of the sample during combustion/pyrolysis. Nitrogen of 99.9% purity at 60ml/min flow rate was set with heating rate of 10°C/min. The STA 409 PC Luxx is a dynamic thermal analyzer that combines both the heat flux

differential scanning calorimetry (DSC) and thermogravimetry (TG). About 30 mg of sample was put in a crucible each time and heated from room temperature to 1000°C. Calculated thermogravimetric output from the TGA software of thermal degradation profile for each sample was obtained as; thermalgravimetric (TG) and differential thermalgravimetric (DTG) curves.

2 Kinetic Parameters Estimation Model

The peak property method (PPM) developed by Kim *et al.* (2004), that the peak temperature (T_m), peak height (H_m), and conversion at peak temperature (α_m) from the TG and DTG curves were utilized to estimate the kinetic parameters, activation energy (E) and pre-exponential factor (A) of a reaction.

The thermolysis of decomposing material can be described to undergo a conversion process from raw material to char and volatiles. The decomposition process can be described by the chemical reaction rate in accordance with Arrhenius law (Trommer, 2004), that is:



Consider the decomposition process as a one-stage chemical reaction, the rate of decomposition is dependent on the temperature (T), and the quantity of reactant, its mathematical expression is given by equation (1).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \dots\dots\dots (1)$$

where α is the conversion of decomposing material, $k(T)$ is the rate constant which depends on temperature, and $f(\alpha)$ represents a conversion function as effect of reactant quantity to the reaction rate.

The function $f(\alpha)$ can be expressed by equation (2).

$$f(\alpha) = (1 - \alpha)^n \dots\dots\dots (2)$$

where n is the reaction order, while the function $k(T)$ is described by Arrhenius equation in accordance with equation (3).

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \dots\dots\dots (3)$$

where A is the pre-exponential factor, E is the activation energy, and R is universal gas constant.

During thermolysis process at a constant heating rate (β),

$$\frac{dT}{dt} = \beta \dots\dots\dots (4)$$

Rearranging Equations (1) to (4), gives equation (5).

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \dots\dots\dots (5)$$

At a peak temperature, the derivative of Equation (5) with respect to temperature, yields zero and allow the following relationship (equation (6)).

$$\frac{E}{nRT_m^2(1-\alpha_m)^{n-1}} = \frac{A}{\beta} \exp\left(-\frac{E}{RT_m}\right) \dots\dots\dots (6)$$

On the other hand, peak height, H_m , is described by equation (7).

$$H_m = \frac{A}{\beta} \exp\left(-\frac{E}{RT_m}\right)(1-\alpha_m)^n \dots\dots\dots (7)$$

The reaction order (n) is approximated using Equation (8) by means of a trial-and-error method, where constant ϕ_a is 0.9440 ± 0.0065 (Kim *et al.*, 2004).

$$n = \frac{\phi_a}{(1-\alpha_m)^{n-1} - (1-\phi_a)} \dots\dots\dots (8)$$

Combining Equation (6) and (7), E and A correlate with the three peak properties (T_m , H_m , and α_m) as follows;

$$E = \frac{nRT_m^2 H_m}{(1 - \alpha_m)} \dots\dots\dots (9)$$

$$A = \frac{H_m \beta \exp(E / RT_m)}{(1 - \alpha_m)^n} \dots\dots\dots (10)$$

Using Equation (9) and (10), *E* and *A* could be estimated.

RESULTS AND DISCUSSION

1 Material Characterization Results

Table 1 presents the proximate, elemental analysis and calorific value of the sampled Scrap tyre and Bagasse. Despite of high volatiles matter content 80.05% for bagasse than 65.05% for scrap tyre as per proximate analysis, the scrap tyre is easily combustible since it contains low moisture content 1.15% than bagasse 9% (Fuel moisture, 2012). There is a significant difference on elemental composition, scrap tyre has higher content of C, H, N and S than that of bagasse, except O. The C and H content are vital for combustion process (Chauhan *et al.*, 2010). The N and S components results to emission of NO_x and SO_x during combustion of the fuel (Hui *et al.*, 2010; Li *et al.*, 2013), which means that bagasse will yield low emission due to low content of these component compare to scrap tyre, despite of higher HHV content in scrap tyre.

2 Thermal decomposition

The thermalgravimetric (TG) and differential thermalgravimetric (DTG) curves of scrap tyre and bagasse, obtained at heating rate of 10°C/min, are presented in Figure 1 and Figure 2, respectively.

Figure 1 shows the thermalgravimetric (TG) decomposition profiles. The profile is presented in three main regions; first region is moisture releases happen at a temperature range of 35 to 110°C, followed by volatiles composite at a range of 180 to 600°C and lastly residue (char & ash) obtained at 600°C and

above. The composite are mainly decomposed within a relatively high and narrow temperature region, suggesting that the decomposition rate is highly sensitive to the temperature.

Figure 2 presents DTG curves for scrap tyre and bagasse. During composite decomposition, all samples exhibited an increase of weight loss towards their maximum value. The weight loss for scrap tyre and bagasse curves shift toward a higher temperature zone. This is because high heating rate affects the temperature gradient between the outside and internal part of the sample (Lv *et al.*, 2010).

Table 1: Proximate and elemental analysis of Scrap tyre and Bagasse results

Parameter	Scrap Tyre	Bagasse
Proximate analysis (% wt as received)		
Moisture	1.15	9.00
Volatile matter	65.05	80.50
Ash	9.87	3.30
Fixed carbon	23.83	16.20
Elemental analysis (% wt at dry basis)		
Carbon	74.15	48.10
Hydrogen	7.47	5.90
Oxygen	6.01	42.40
Nitrogen	0.40	0.15
Sulphur	3.23	0.02
HHV (MJ/kg)	27.19	17.33

Bagasse like other biomass is mainly composed of hemicelluloses, cellulose and lignin (Osorio *et al.*, 2006). Its DTG has two major peaks, the former is a peak resulting from hemicelluloses at 294°C, the latter results from cellulose at 320°C. However, decomposition of lignin does not have a significant behaviour as the other two compounds, its maximum decomposition rate overlaps with that of cellulose (Gašparović *et al.*, 2012). The contribution of lignin decomposition is the tail part of bagasse decomposing materials, because at these temperatures,

both hemicellulose and cellulose are already decomposed.

The major composite materials of scrap tyre are carbon black, elastomers and processing oils. Its DTG curve has three stages of degradation easily recognized on Figure 2, the first stage of degradation (210-400°C) to the evaporation of oil/plastizer included in the tyre with peak at 330°C. The second and third stages

correspond to the degradation of elastomers at peak of 468°C (Scrap tyre pyrolysis, 2012).

3 Kinetics of thermal decomposition

Table 2 shows the estimated kinetic parameters calculated from Equation 9 – 10, using TG and DTG data obtained at peak properties, assuming first order reaction of decomposing sample composite.

Table 2: Kinetic parameters of the scrap tyre and bagasse

	Scrap tyre		Bagasse	
	oil	elastomer	hemicellul	cellulose
Peak temperature T_m (K)	603	741	567	593
Peak height H_m (K^{-1})	0.0034	0.0066	0.028	0.005
Conversion at peak temperature	0.75	0.25	0.58	0.22
Activation energy E (kJ/mol)	41.113	39.31	178.191	18.741
Pre-exponential Factor (A)	495.5	56	1.74×10^{16}	2.87

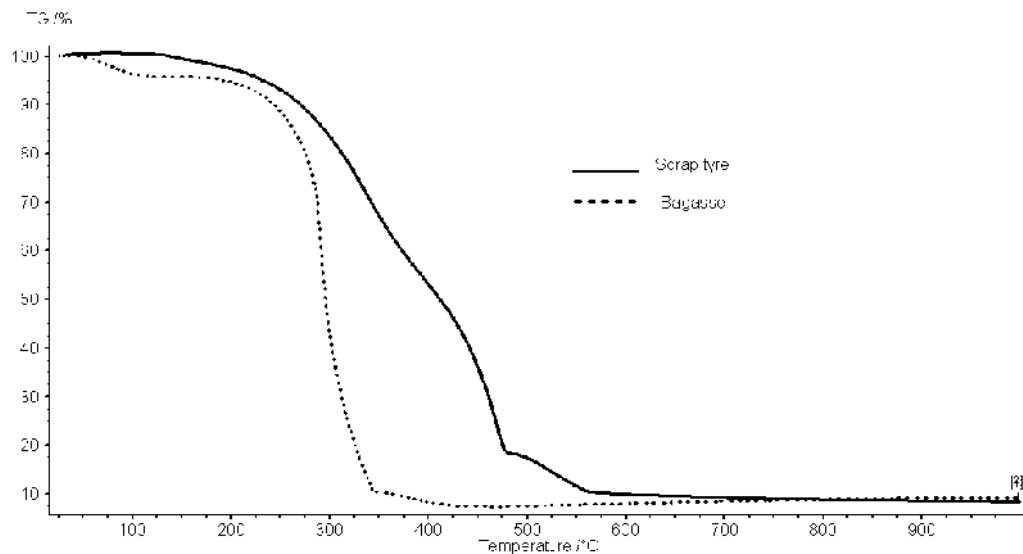


Figure 1: TG curves for scrap tyre and bagasse at 10°C/min

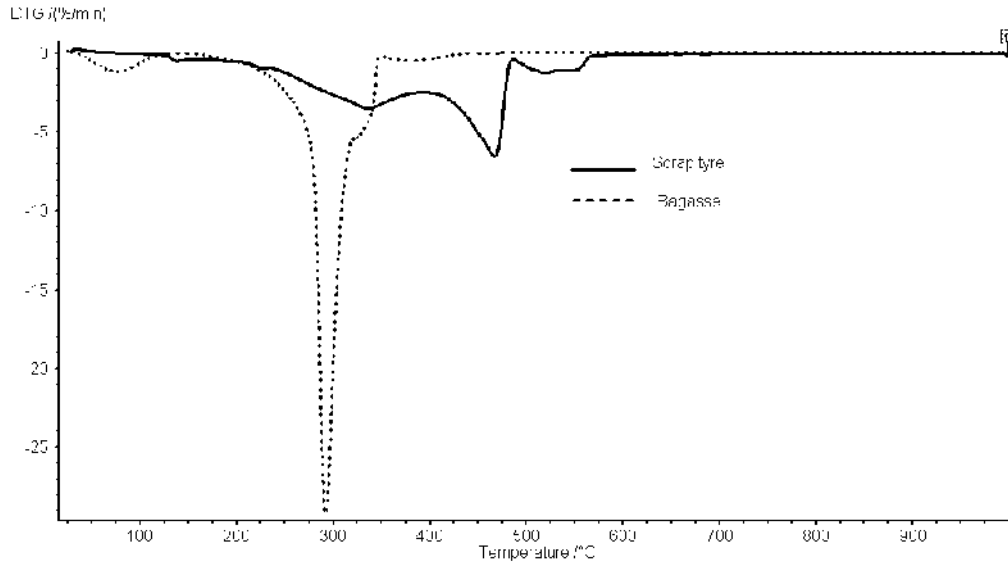


Figure 2: DTG curves for scrap tyre and bagasse at 10°C/min.

CONCLUSIONS

Thermogravimetric analysis was used to investigate the resources potential in energy applications; and to obtain kinetics information from the reaction mechanisms during devolatilization. The elemental analysis shows that bagasse has small composition of nitrogen and sulphur elements less than 2%, which will result into low emission of NO_x and SO_x when combusted compared to scrap tyre. However, the bagasse has high content of oxygen, which means it has low energy content compare to scrap tyre. The TG analysis of the sampled species has a large number of volatiles 84.21% of bagasse and 85.05% of scrap tyre, which suggest all of them are suitable for pyrolysis or gasification process. Simultaneously, the ash production of scrap tyre is generally higher than bagasse biomass in both proximate and TG analysis, which is an indication the fuel is suitable for gasification or combustion. Scrap tires make an excellent fuel due to relatively higher HHV 27.19 MJ/kg than bagasse 17.33 MJ/kg. With this regard scrap tyre is most useful in thermal conversion systems.

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NOMENCLATURE

A	pre-exponential factor
DSC	differential scanning calorimetry
DTG	differential thermalgravimetric
E	activation energy
HHV	higher heating value
H_m	peak height
n	reaction order
R	universal gas constant
TG	thermogravimetry
TGA	thermogravimetric analyzer
T	temperature
T_m	peak temperature
α	conversion of decomposing material,
α_m	conversion at peak temperature
β	constant heating rate

$k(T)$ rate constant
 $f(\alpha)$ conversion function
 \emptyset_a constant 0.9440 ± 0.0065

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