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THERMOGRAVIMETRIC AND KINETIC STUDIES ON PALM SHELLS

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ABSTRAK : *Pada masa ini, disebabkan kepekaan alam sekitar dan ekonomik, minat dalam penggunaan biojisim untuk menghasilkan tenaga dan bahan kimia telah menarik perhatian. Malaysia merupakan pengeluar minyak sawit terbesar di dunia juga menghasilkan bahan buangan yang banyak. Untuk menggunakan bahan buangan ini secara efektif, penggunaan kaedah pirolisis merupakan satu teknik yang terbaik. Dalam kajian ini, pada awalnya, pirolisis bahan buangan tempurung kelapa sawit dijalankan dengan menggunakan analisis termogravimetrik (TGA). Kesan kadar kepanasan pada sifat pirolisis dikaji untuk serbuk kelapa sawit bersaiz 300 and 600 μm. Parameter kinetik juga dikaji untuk kadar kepanasan yang berbeza.*

Kertas kerja ini juga menerangkan keputusan dari radas skala makmal sebuah lapisan terbendalir 'circulating' (CFB), yang telah dipasang di SIRIM Berhad, Shah Alam. Ia sesuai untuk ujikaji gasifikasi dan pembakaran bagi biojisim yang berlainan. Dengan menggunakan radas ini, satu kefahaman mengenai kesan aliran udara utama dan kadar suapan kepada pencemaran telah diperolehi. Kajian ujikaji juga dibuat untuk pengaruh suhu terhadap pirolisis. Kepekatan emisi CO, NO_x and CO_2 dari gas serombong juga dikaji. Prestasi pembakaran telah dikaji dengan perubahan pada aliran udara ke ketuhar CFB. Emisi NOx adalah dari julat 38-75 ppm manakala emisi CO didapati tinggi untuk kadar aliran udara utama yang tinggi.

KATAKUNCI: *Analisis termogravimetrik (TGA), bahan buangan kelapa sawit, biojisim, emisi, kinetik, pirolisis*

ABSTRACT : Recently, owing to environmental and economic considerations, interest in utilising biomass for the production of energy and chemicals is increasing. Malaysia being the largest producer of palm oil has huge amount of oil palm wastes. In order to utilise these wastes efficiently, pyrolysis is emerging as a promising thermo-chemical technique. In this study, pyrolysis of oil-palm shell waste was carried out using thermogravimetric analysis (TGA). The effects of heating rate on the pyrolytic properties were investigated for palm shell powder of 300 and 600 μm particle size. Kinetic parameters were also determined for different heating rates.

This paper also describes the results from a bench-scale Circulating Fluidised Bed (CFB) test rig, installed at SIRIM Berhad, Shah Alam, suitable for gasification and combustion experiments using different biomass materials. Using this rig, a better understanding of the effect of primary flow and feeding rate on the emission behaviour was established. Experimental studies were also done to investigate the influence of temperature on pyrolysis. The concentrations of CO, NOx and CO_2 in the flue gas were measured. The combustion performances were evaluated by varying the primary gas flow through the CFB tubular furnace. The emission of NOx ranged from 38-75 ppm while the CO emissions were high for higher primary air flow rates.

KEYWORDS : Biomass, emission, kinetics, oil palm wastes, pyrolysis, Thermogravimetric analysis (TGA)

INTRODUCTION

Palm oil and its liquid fraction, palm olein, are consumed worldwide as cooking oils and constituents of margarine and shortening. During oil palm planting and processing, a large amount of solid wastes such as palm trunks, palm fronds and empty bunches are generated. Malaysia, being the largest producer of palm oil in the world, generates a significant amount of oil palm wastes. In January 2005, the production of palm oil is about 13.97 million ton and the total solid wastes generated by this industry amounted to more than 3.6 million ton (PORIM, 2005). For every 100 kg of crude palm oil produced during the oil palm milling process, 52 kg fibre, 22 kg shell and 85 kg empty fruit bunch are generated. There are more than 350 palm oil mills in the country. Each plant is equipped with at least a boiler and two incinerators. Palm oil mills are a self sufficient industry as far as energy utilisation is concerned. The palm fibres and shells generated as waste are used as boiler fuel in the mills (Ma *et al.*, 1999; Jamil *et al.*, 1999).

Biomass, as a fuel, is characterised by high moisture and volatile content, low bulk density, low specific energy and normally low ash content. The proximate and ultimate analysis of some biomass fuels are shown in Table 1 and Table 2 and they are compared with palm shell (Ani, 1992).

Palm shell waste is generated from oil palm milling process. Fresh fruit bunches contain (on fresh weight) about 19% palm oil, 6-7% kernel, 14-15% fibre, 6-7% shell and 21% empty fruit bunch material (EFB). The energy content of the palm shell varies according to the moisture and residual oil content. Its high specific energy content is of interest when compared with the oil palm fibres or EFB. Oil palm shell waste contain around 67-80% of volatile matter compared to 40% to that of coal.

Table 1. Proximate analysis of different biomass

Solid Waste	Proximate Analysis %			
	Moisture	Volatile	Fixed carbon	Ash
Palm Shell	9.7	67	21.2	2.1
Rice Husk	12.0	52.4	17.1	18.5

Table 2. Ultimate analysis of biomass in Malaysia

Solid Waste	Ultimate Analysis %					GCV MJ/kg
	C	H	N	O	S	
Palm Shell	47.62	6.2	0.7	43.38	-	19.1
Rice Husk	38.2-55.8	0.2-0.31	1.7-1.0	29.9-31.7	0.07-0.12	12.1-19.0

Amongst the thermochemical conversion processes (e.g. pyrolysis, gasification and combustion), pyrolytic process is recognised as the most promising since it can be used either as an independent process for fuels and other valuable chemical products or an initial step to gasification or combustion (Bridgwater *et al.*, 1988; Grassi *et al.*, 1990). Development of proper thermochemical conversion using the pyrolytic process for oil-palm solid wastes, and the design and operation of related equipment require the determination of kinetic parameters (i.e., activation energy, frequency factor and reaction order) and a detailed understanding of the pyrolytic mechanism (Guo *et al.*, 1999; Lua *et al.*, 2000)

In this paper, pyrolysis of palm shell was carried out using thermogravimetric analysis (TGA). The effects of raw material particle size, pyrolytic temperature and heating rate on the pyrolytic properties (for example, the shape of thermograms) were investigated to determine the main factors of the pyrolytic process.

The experimental thermo chemical study of the oil palm shell waste was done in a circulating fluidised-bed combustor (CFBC) using alumina particles as inert material. The main objectives of this study were to establish the formation and reduction of major gaseous pollutants (CO and NO) in the CFBC when firing selected biomass fuels, and to determine the combustion performance when fired at different operating conditions.

MATERIALS AND METHODS

The oil-palm shells were obtained from a palm oil mill in Kulai, Johor, Malaysia. As-received palm shells were dried to remove free moisture absorbed during land dumping. The pre-dried samples were crushed and sieved to several size fractions. The pyrolysis of palm shell was carried out using a Thermogravimetric analyzer (Perkin Elmer Pyris TGA-7). Approximately, 20 mg sample was placed in an aluminum pan. The furnace was heated from ambient temperature to 990°C at constant heating rates (25 and 80°C/min). Purified nitrogen (99.9995% purity) at a constant flow rate was used as the purge gas to provide an inert atmosphere for pyrolysis and to remove any gaseous and condensable products evolved, thus minimising any secondary vapour-phase interactions. The sample was heated by both radiation from the furnace wall and convection of the purge-gas flowing through the furnace chamber. The sample weight was measured continuously using a microbalance as a function of time or temperature.

The thermochemical experiments were carried out at SIRIM Berhad, Shah Alam in Malaysia. The system is developed by JFE, Japan under a joint venture programme with the Japanese government through NEDO/METI. The experimental apparatus consists of a circulating fluidised bed type experimental gasifier, experimental sample supplying unit, secondary combustion furnace, gas cooler, dust collector, blower and control panel. A schematic diagram of the test rig is shown in Figure 1.

The circulating fluidised bed (CFB) experimental gasifier is a vertical tubular furnace having an inner diameter of about 50 mm and a height of 2000 mm. The fluidising air supplied from the furnace bottom and the circulating particles are separated from air by the cyclone and the particles returned through the loop seal on the downstream side of the furnace. The furnace is provided with three external electric heaters (upper, center and lower), which enable temperature control in the furnace. A heater is also installed in the air supply line to preheat air.

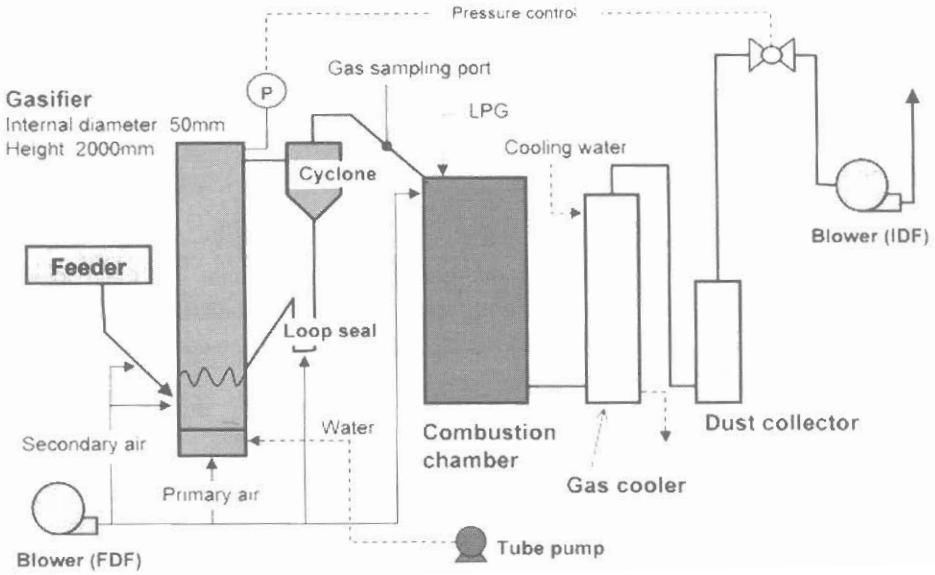

Figure 1. *Layout of the experimental CFB gasifier at SIRIM Berhad*

A sampling port is provided in the middle of the duct. Gas, tar and moisture generated through gasification can be sampled through the hole. For monitoring the gasification condition, the concentrations of CO, CO_2 and O_2 in the produced gas were measured with a gas analyser.

The palm shell powder of 300 μm is fed into the gasifier through a screw feeder and rotary valve. The feed rate from the screw feeder can be adjusted by changing the rotational speed of the driving motor through an inverter control. The rotary valve is located after the screw feeder to control the seal of the gasifier. Immediately before the induction fan (IDF), an automatic valve is connected to the differential pressure gauge that measures the pressure in the furnace. The valve controls the pressure in the furnace during the experiments. The operation of the following devices; heater temperatures, air preheat temperature, in-furnace pressure and sample feed rate are controlled on the main control panel.

The temperatures at various locations in the CFB rig were continuously monitored and recorded using Yokogawa Hybrid Recorder (HR 1300). The furnace pressure and supply air flow rate were also monitored. The concentrations of CO, CO_2 and O_2 contained in the emission gas were also monitored and recorded using Madur Flue Gas Analyzer (GA-40 plus). The operating parameters of CFB test rig are shown in Table 3.

Table 3. Experimental operating conditions of the CFB test rig

EFB feed rate		2.4-60 kg/hr
Palm shell powder feed rate		3.0-7.0 kg/hr
Gasifying agent flow rates	Primary air	1.0-3.5 m^3/hr
	Secondary air	1.0-1.5 m^3/hr
	Loop seal air	0.1-0.75 m^3/hr
	Combustion air	24-28 m^3/hr
Gas velocity		1.0-2.0 m/s
Gas residence time		1.1-2.0 sec
In-furnace temperature		600-850°C

DETERMINATION OF KINETIC PARAMETERS

Thermogravimetric data is used in characterising the fuel as well as in investigating the thermodynamics and kinetics of the reaction and transitions that result from the application of heat to the samples. TGA is useful in providing kinetic data as a function of various reaction parameters such as temperature and heating rate (Ismail *et al.*, 1999). Currently several methods are available in the literature that can be used to calculate kinetic parameters (Guo *et al.*, 2001).

The rate of reaction is given by:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha)^n \qquad (1)$$

where A (min-1) is the frequency or pre-exponential factor of the pyrolytic process, E (J/mol) is the activation energy of the pyrolytic process, R (J/mol K) is the universal gas constant, T (K) is the absolute temperature, n is the order of reaction, t is the time, and α is the fraction of reactant decomposed at time t (min).

The fractional reaction α is defined in terms of change in the mass of the sample,

$$\alpha = \frac{w_o - w}{w_o - w_f} \qquad (2)$$

where w_o, w, w_f are the initial, actual and final weights (mg) of the sample, respectively.

In order to determine the values of kinetic parameters, the integral method is used to solve Equation (1).

For constant heating rate β, where:

$$\beta = \frac{dT}{dt} \tag{3}$$

Equation (1) can be expressed by the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} (1-\alpha)^n \tag{4}$$

Rearranging and integrating Equation (4), the following expression can be obtained:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{A}{\beta} \int_o^T e^{-E/RT} dT \tag{5}$$

Since $\int e^{-E/RT} dT$ has no exact integral, $e^{-E/RT}$ can be expressed as an asymptotic series and integrated, with the higher order terms ignored.

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\beta E}\left[1-\frac{2RT}{E}\right]e^{-E/RT} \tag{6}$$

Expressing Equation (6) in logarithmic form

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]\right] - \frac{E}{RT} \quad (for\ n \neq 1) \tag{7}$$

if 2RT/E << 1 is assumed, Equation (7) becomes

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (for\ n \neq 1) \tag{8}$$

If n=1, the following equation can be used

$$\ln\left[\frac{-\ln-(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (for\ n = 1) \tag{9}$$

Thus, a plot of

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] versus \frac{1}{T} \quad (for\ n \neq 1) \tag{10}$$

or

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] versus \frac{1}{T} (for\ n = 1) \quad (11)$$

should result in a straight line of slope –E/R for the proper value of n. The criterion used for the acceptable values of E and A is that the final value of n should yield the values of E whose linear correlation coefficient are the best.

RESULTS AND DISCUSSION

Figure 2 shows the residual weight fractions of two different particle size palm shell powder undergoing pyrolysis at the heating rates of 25 and 80°C/min. The figure presents the typical plots of the thermal events observed during pyrolysis. It should be noted that each thermal event is defined as the region where the slope of TGA curve is constant. A major shift in the slope of the TGA curve was thus treated as the end of a thermal event and commencement of another new thermal event. The thermograms for the two particle sizes showed that as the heat wave propagates into the solid, inherent moisture evaporates and this ends at about 130°C. This is represented by 'Thermal Event 1' in Figure 2. As the temperature is further increased, the breakdown of more stable polymers begins. For the two different palm shell powders, the thermograms showed that pyrolysis commences after approximately 260 °C. Subsequently significant weight loss occurred indicating the occurrence of main decomposition. These are represented by 'Thermal Event 2' and 'Thermal Event 3' respectively.

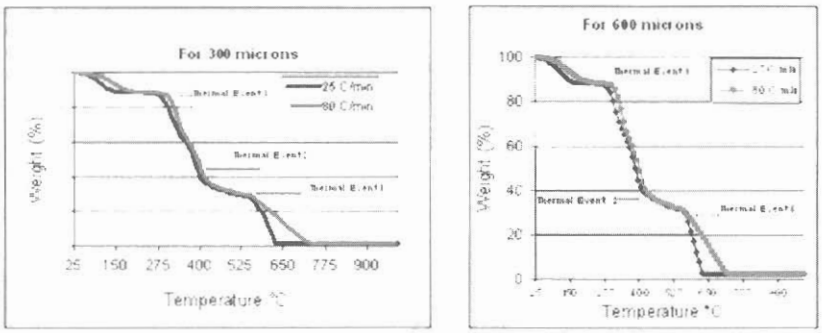

Figure 2. *TGA analysis of weight loss (%) for two different particle size palm shell powder*

At the beginning, CO_2 and CO were released as the main gaseous products while during the main decomposition period, a large amount of CO_2, CO, H_2 and hydrocarbons (i.e. CH_4; C_2H_4; C_2H_6) were released, resulting in the significant weight loss.

The heating rates influenced the shape of the TGA curve. When a sample decomposes, then the vapour pressure of the gaseous products exceeds the ambient partial pressure. At lower heating rates the sample temperature is more uniform and diffusion of the gaseous product can occur throughout the sample. However, when the heating rate is increased such free diffusion is inhibited and the decomposition temperature is increased. It was also observed that at lower heating rates the decomposition atmosphere is more uniform and the decomposition reaction is completed within a narrower temperature interval.

Figure 3 shows the residual weight fractions during pyrolysis of palm shells at two heating rates. It can be seen that there is an obvious lateral shift in the thermograms for different heating rates. The heating rates also affect the total weight loss. As the heating rate increased, a faster pyrolytic reaction occurred resulting in higher pyrolytic conversion to volatile species.

In Figure 3, the main decomposition was essentially completed by an elapsed duration of 9 min and 24 min for heating rates of 80 and 25°C/min, respectively.

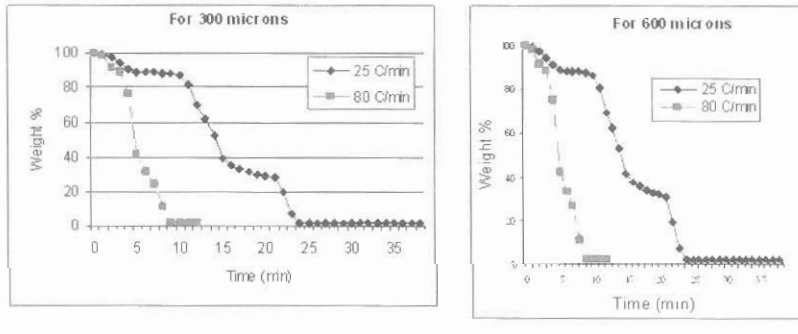

Figure 3. *TGA analysis of weight loss (%) for different heating rates*

From Figure 3, it can be inferred that the pyrolysis of oil palm shell waste is primarily controlled by reaction kinetics which is in turn highly dependent on the reaction temperature. In other words, the pyrolysis is controlled by both heat transfer and chemical reaction. At a lower heating rate, a relatively lower pyrolysis rate was observed resulting in a lower conversion ratio.

Figures 4 and 5 show the derivative thermograms (dm/dt) for the pyrolysis of oil palm shell waste powder of 300 and 600 μm particle size at the two different heating rates. The height of the peak at any temperature gives the rate of mass change at that temperature. Figures 4 and 5 showed that for the heating rates 25 and 80°C/min, the maximum decomposition rates are 15 and 50 mg/°C, respectively. The decomposition rates are identical for different particle sizes as particle sizes below 2 mm are primarily considered as fine particles and their pyrolysis is purely controlled by reaction kinetics. It can be clearly seen that there exists separate steps of reactions that took place at distinct temperature regimes with obvious maximas for

different heating rates. The heating rate had influenced not only the maximum rate of pyrolysis and its temperature, but also the starting and ending temperatures for the pyrolytic process. This phenomena is also confirmed by the fact that there was a lateral shift to higher temperatures during pyrolysis as the heating rate was increased.

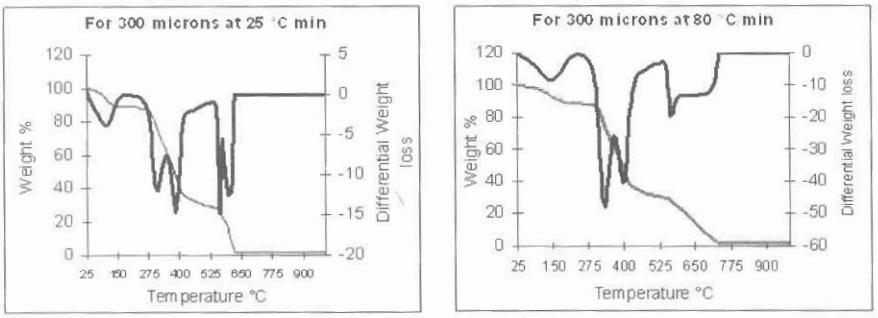

Figure 4. *DTG for 300 μm size oil palm shell waste at different heating rates*

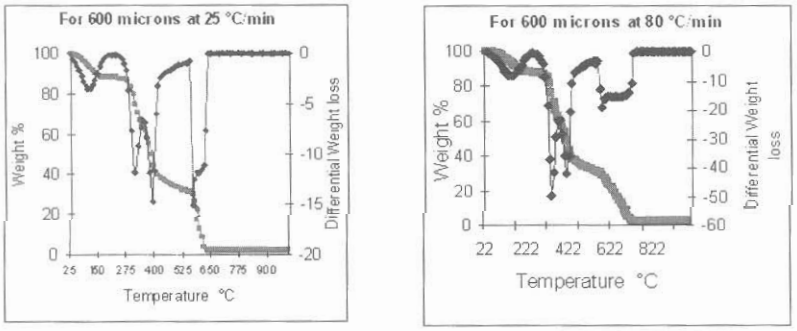

Figure 5. *DTG for 600 μm size oil palm shell waste at different heating rate*

In order to determine the values of the kinetic parameters, the integral method is used and a plot of $\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$ *versus* $\frac{1}{T}$ *(for* $n = 1$*)* that results in a straight line of slope (– E/R) for n=1 is obtained. The criterion used for acceptable values of E and A is that the linear correlation coefficients are the best. The basic assumptions involved are that the reaction is purely kinetic controlled and pyrolysis follows a first-order reaction.

Using data from the pyrolysis thermograms (Figure 2), the kinetic parameters, the activation energy (E) and the frequency factor (A), were estimated using Figures 6 and 7 with high correlation coefficients (all above 0.94) as listed in Table 4. For all the heating rates, the first-order reaction mechanism applies for the pyrolysis of palm shells. As the heating rate increased, the activation energy changed insignificantly but the frequency factor was dependent on the heating rate,

increasing progressively from 6.8 x 10^3 to 6.2 x 10^4 sec^{-1} for 300 μm particles. This suggested that the higher the heating rate, the easier and faster the pyrolytic reaction. These parameters can be used to predict the time-conversion profiles for the pyrolytic process at different heating rates. A similar pyrolytic behaviour can be seen for the 600 μm particles.

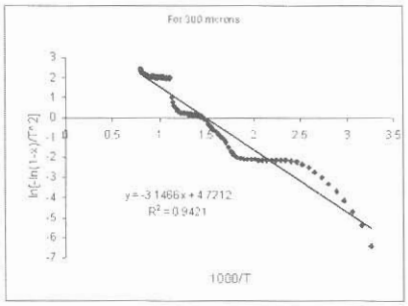

Figure 6. *Kinetic plot of 300 μm particle at the heating rate of 25 °C/min*

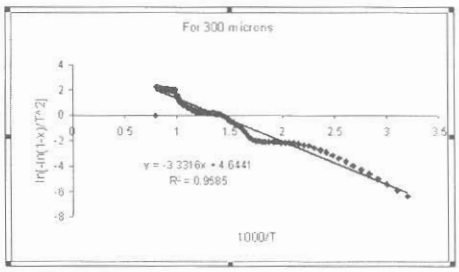

Figure 7. *Kinetic plot of 300 μm particle at the heating rate of 80°C/min*

Table 4. Kinetic parameters for the pyrolysis of palm shells

Particle Size	Heating Rate	Activation Energy (kCal/mole)	Frequency Factor (sec^{-1})
300 μm	25°C/min	26.16	6.8 x 10^3
	80°C/min	28.01	6.2 x 10^4
600 μm	25°C/min	22.98	2.7 x 10^3
	80°C/min	29.03	6.8 x 10^3

The thermochemical studies of palm shell waste of 212-300 μm particle size were also carried out in the CFB test rig at SIRIM Berhad. The experimental conditions used were similar to those stated in Table 3. It was found that the palm shell particles were too small and they were easily pushed by the screw feeder even at a low rpm. This caused a heavy flow of fine palm shell particles into the furnace.

The temperature at the top of the CFB increased rapidly as the feeding started and reached to ~ 709°C in a very short time as shown in Figure 8. In order to evaluate the effect of primary airflow through the CFB, the flow rate was varied and the system was stabilised before data was recorded. The emission and experimental data are shown in Table 5.

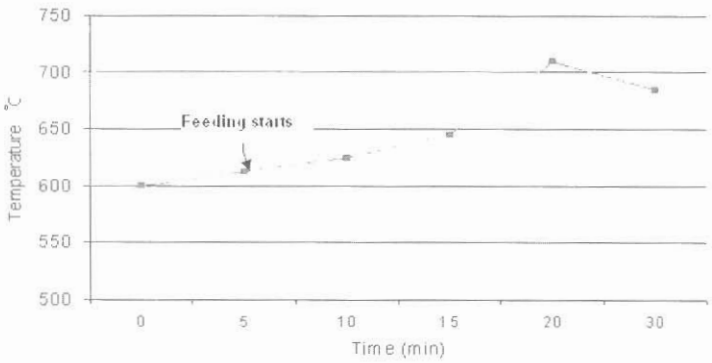

Figure 8. *Variation of CFB temperature with time*

Table 5. Emission data for variation in primary air

Sr. No.	Primary Air Flow rate m^3/hr	Exhaust Temp. °C	$\%CO^2$	CO ppm	NOx ppm	CFB Top Temp. °C
1.	1.0	185	9.58	2950	75	709
2.	1.5	160	9.19	4819	49	685
3.	2.0	150	8.29	7000	38	680

Due to increased particle flow rate, the circulating particle forms a dense bed. Palm shell particles fed to this layer contact with the high-temperature circulating particles and are quickly pyrolysed. The contact between the palm shell particles (PSP) and the circulating particles of higher temperature improves the heat conductance to the PSP and improves and enhance the rate of pyrolysis. As shown in Table 5, as the primary airflow increased, the CO concentration also increased rapidly. This is probably due to the very fine particle size of the PSP and the low residence time in the CFB furnace resulting in poor combustion and a high concentration of CO near the top of the CFB. The emission was characterised by heavy white smoke representing incomplete combustion and enhanced CO formation.

CONCLUSION

Based on the thermogravimetric analysis, pyrolytic temperature and heating rate were found to have significant influence on the pyrolysis of oil-palm shell. The two-stage reaction characteristic

was confirmed by the obvious maxima in the derivative thermogram (DTG) for pyrolysis of palm shells under different heating rates. The DTG curves suggest that heating rates do affect the decomposition rates. As the particles were primarily fine particles, the pyrolysis was not affected by particle size and was controlled instead by pure reaction kinetics. It could be clearly seen that there existed separate steps of reactions that took place at distinct temperature regimes with obvious maxima for different heating rates. Kinetic parameters (activation energy and frequency factor) were obtained by curve fitting the experimental data.

The gasification experiment was successfully conducted using the CFB test rig. Gasification of oil palm shell waste produced gas containing H_2, CO and CH_4 produced. The relationship between in-furnace temperature and primary airflow on the emission characteristic was identified.

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