

## Kinetics of Devolatilization of Oil Palm Solid Wastes Using Thermo-Gravimetric Analysis

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### ABSTRACT

*The kinetics of the devolatilization of oil palm fibres and shells have been determined in a Thermo-Gravimetric Analyser (TGA). The TGA data indicate that the devolatilization process begins around 200°C and terminates around 600°C. The Differential Thermal Analysis (DTA) data indicate the existence of two different rates of devolatilization with the turning point at around 350°C. The temperature at which the maximum rate of weight loss occurs are around 315°C and 380°C. The kinetic parameters, namely the activation energy and the frequency factor, are determined assuming a first order reaction. The data are compared to that of pure cellulose.*

### ABSTRAK

*Kinetik penyahmeruapan sabut dan tempurung kelapa sawit telah ditentukan dengan sebuah analisis permeteran graviti haba (TGA). Data dari TGA menunjukkan proses penyahmeruapan bermula pada suhu sekitar 200°C dan berakhir sekitar 600°C. Data dari analisis haba kebezaan (DTA) menunjukkan kewujudan dua kadar penyahmeruapan yang berbeza dengan titik pusing sekitar 350°C. Suhu dimana kadar kehilangan berat mencapai maksimum adalah sekitar 315°C dan 380°C. Parameter kinetik, yakni tenaga pengaktifan dan faktor frekuensi, telah ditentukan dengan anggapan tindakbalas tertib pertama. Data yang didapati telah dibandingkan dengan data untuk selulosa tulen.*

### INTRODUCTION

The milling process involved in the palm oil industry produces large amounts of solid waste. These solid wastes, which are in the form of empty fruit bunches (EFB), fibres and shells, represent approximately 50 percent of the original fresh fruit bunches. It is estimated that the total production of palm shells and palm fibres by the Malaysian palm oil industry in 1990 will be 1.31 and 2.27 million tonnes respectively [1].

The palm oil industry is indeed very fortunate in the sense that these biomass wastes from the milling processes can be conveniently used as boiler fuels. The industry does not have to depend on other sources of fuels for energy to run its processes and thus is of immense advantage economically and technically to the industry. However, due to systems inefficiency, and avail ability of surplus supply, about 30% of these biomass are wasted [2,3].

Shortages and the upward spiral in oil prices have given impetus to research on finding new sources of energy, of which biomass is one such renewable that has merited attention. Successful utilization of the wasted biomass in the palm oil industry by conversion into more useful and valuable products may bring a new dimension to the industry.

Thermochemical processes such as pyrolysis and gasification at atmospheric pressure have been proposed for converting biomass materials into useful energy products. When cellulosic materials are heated to high temperatures in the absence of oxygen, a series of chemical reactions takes place that results in evolution of volatile products and a carbonaceous solid residue. These reactions take place in two principal steps: the first is devolatilization which produces volatile matters and char, and the second consists of secondary reactions involving the evolved volatiles in the gas phase and the solid char [4].

Thermal analysis is one of the most commonly used methods for studying devolatilization. Thermogravimetric analysis (TGA) of pure cellulose, newsprint, hardwood, softwood and cow manure were carried out by Antal et al. [4]. Havens et al. [5] performed TGA and differential scanning calorimeter studies of the pyrolysis of wood. Barooah and Long [6] investigated the rates of pyrolysis of materials such as sawdust, granular cellulose, and sucrose-impregnated pumice, using a bench-scale fluidised bed operating with nitrogen as the fluidizing gas. Raman et al. [7] carried out devolatilization studies on feedlot manure using TGA. A thermochemical study of wood pyrolysis and char gasification reactions was carried out by Haff and Sheena [8].

The objectives of the present work were:

1. to study the devolatilization characteristics of palm shell and palm fibres with a TGA, and
2. to determine kinetic parameters for the devolatilization reaction.

## EXPERIMENTAL

Thermogravimetric analysis of palm fibre and shell were carried out using a Stanton Redcroft 280 Series Thermogravimetric Analyser. This apparatus provides for the continuous measurement of sample weight as a function of temperature over the range ambient to 1000°C. Samples, approximately 20 mg, can be heated at a rate up to 80°C min<sup>-1</sup> and provision is made for an electronic differentiation of the weight signal to give the rate of weight loss. The thermogram and the rate of weight loss are recorded continuously.

Palm shell and fibre samples from the Federal Land Development Authority (Felda) Air Tawar 3 mills, in Kota Tinggi, Johore, Malaysia were used in this investigation. The samples were air-dried before subsequent preparation. The shells were ground into small particles from their original sizes of between 1.5 cm to 3 cm. Sieves were used to separate the sample into various size ranges, of which -0.500 mm to + 0.353 mm size range was used in this investigation. The fibres, with thickness between 0.3 mm to 1.0 mm, were chopped down to between 3 mm to 10 mm length.

The devolatilization experiments were carried out in a nitrogen atmosphere by placing a sample of about 20 mg on the sample pan. A purge gas flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$  was employed. The sample was heated from ambient to  $600^\circ\text{C}$  at preset heating rates of 25, 40 and  $80^\circ\text{C min}^{-1}$ . Typical ultimate analyses of the palm fibre and shell used in this investigation are presented in Table 1.

In order to give a better understanding, the thermograms of palm shell and fibre are compared to that of pure cellulose. (Whatman Paper No. 1). Approximately 20 mg of pure cellulose samples were devolatilised in the TGA following the same procedure and experimental conditions as the palm shell and fibre.

TABLE 1. Typical ultimate analysis of palm shell and fibre

	Weight % (Dry Basis)	
	Shell	Fibre
Carbon	49.7	45.7
Hydrogen	5.8	5.7
Nitrogen	0.6	1.0
Sulphur	0.2	0.3
Oxygen	41.7	40.8
Ash	2.0	6.5

## RESULTS AND DISCUSSIONS

Figure 1 shows typical thermograms for palm shell with size range  $-0.500 \text{ mm}$  to  $+0.353 \text{ mm}$ , palm shell and a cellulose material (Whatman Paper No 1). These thermograms were obtained at a heating rate of  $40^\circ\text{C min}^{-1}$ , a nitrogen purge gas rate of  $50 \text{ cm}^3 \text{ min}^{-1}$ , and at maximum devolatilization temperature of  $600^\circ\text{C}$ .

The thermograms obtained clearly show in all cases two regions of weight loss for palm shell and fibre. The first region is due to evaporation of the inherent moisture of the samples, which represents approximately 4.5% for the shell and fibre samples and 4.0% for the cellulose material. The release of moisture in all cases corresponds to the first peak in the derivative of thermal analysis (DTA) curves, within the temperature range of 60 to  $170^\circ\text{C}$ , as shown in Figure 2.

The second region represents the active devolatilization process. As can be seen, the devolatilization of palm shell and fibre starts around  $200^\circ\text{C}$  and is virtually complete around  $600^\circ\text{C}$ . The evolution of volatile matter in all cases for the palm shell and fibre is characterised by the presence of two peaks in the DTA curves as shown in Figure 2. Similar characteristics were observed by Dupont [9] for rice husks. The maximum

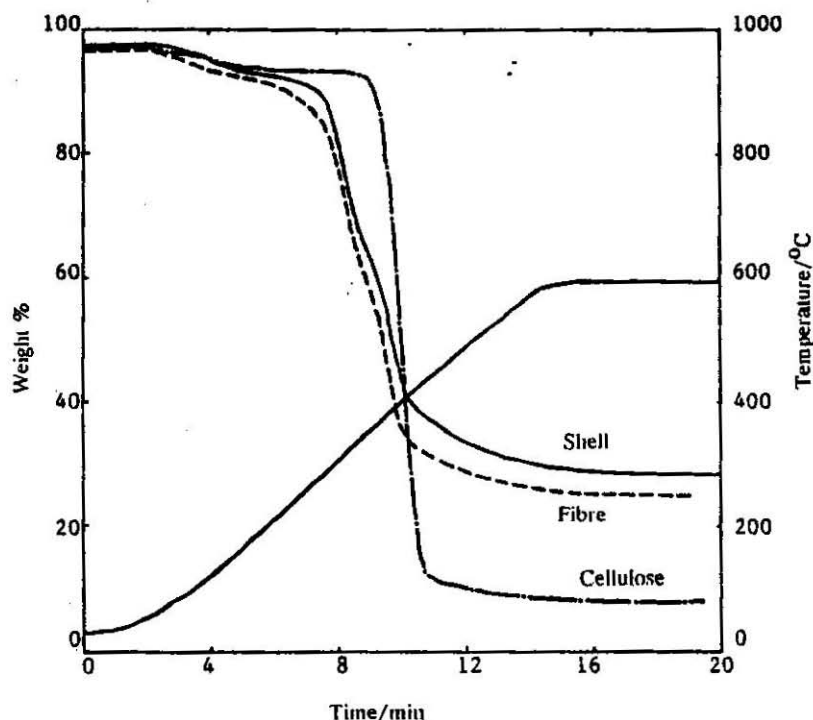


FIGURE 1. Thermograms for palm shell, fibre and a cellulose materials obtained at  $40^{\circ}\text{C min}^{-1}$  heating rate, heated to  $600^{\circ}\text{C}$  and a nitrogen purge gas rate of  $50\text{ cm}^3\text{ min}^{-1}$

rate of weight loss always occur around 80% for the first peak and 50% for the second for both fibre and shell. In contrast, the DTA curve for the cellulose material only shows one peak in the devolatilization stage. In this case, the devolatilization process begins at around  $360^{\circ}\text{C}$  and virtually complete at around  $450^{\circ}\text{C}$ .

Preliminary results and the kinetic parameters obtained from the devolatilization studies of palm shell and fibre are summarised in Table 2. The following observations can be made from these data without going into the basic chemistry of the reactions involved:

1. There is a consistent lateral shift in the thermograms for both shell and fibre with respect to the heating rate. This observation agrees with the previous studies by Havens [5] on wood pyrolysis, Antal et al. [4] on pure cellulose, newsprint, wood and cow manure, Raman et al. [7] on feedlot manure, and Boateng et al [10] on rice hulls.
2. The yields of char and volatile matter, based on dry and ash free, for both fibre and shell are not affected by the heating rates. However, the yields of volatile matters from palm fibre are higher than that of the shell. This could be due to some oil remaining in the shell due to the inefficiency of the mechanical press process for extracting the oil in the mills.

3. The activation energy is estimated with the assumption of a first order reaction. There are two different values of activation energies obtained which are reflected in the two maxima from the DTA curve in Figure 2. The low value activation energy is related to the first peak in the devolatilization stage and the higher value is for the second peak. In both cases, the activation energies increase with increasing heating rates. This observation contradicts with the observation made by Raman et al. [7] who found that the activation energy was not affected by the heating rate.

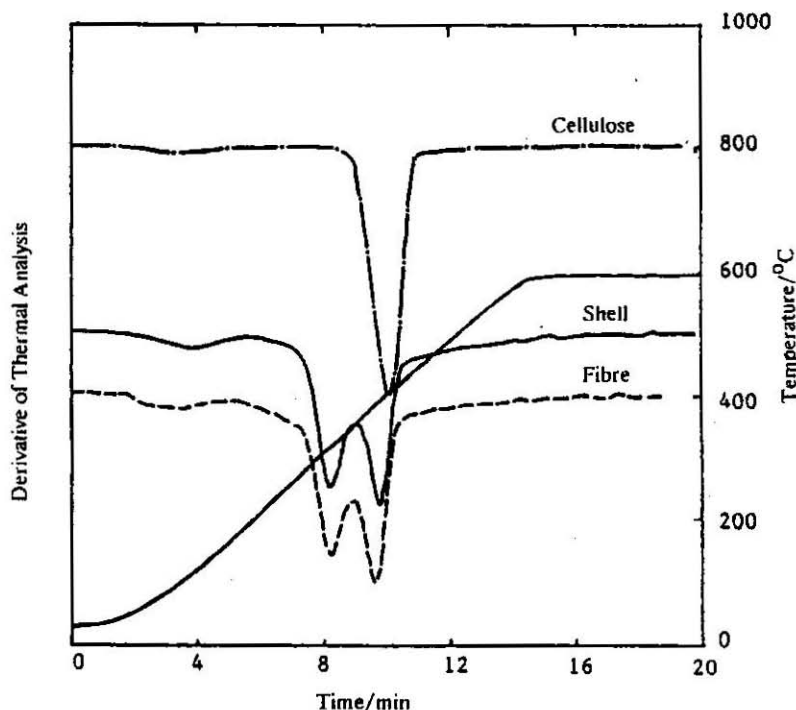


FIGURE 2. DTA Curves for palm shell, fibre and a cellulose material (The position of the DTA curves are purposely offset to give clear indication of the shape of the curves)

The observations tend to prove the existence of two different groups of reactions taking place in distinct temperature regions. Figure 1 and Figure 2 suggest that the second group of reactions corresponds to degradation of cellulose as shown by the coincidence between the peak for cellulose and the second peaks for both fibre and shell in the DTA curve. The first peak could be due to the degradation of different type of material available in the shell and fibre. In an earlier study on rice straw, having the composition of hemicellulose 24.5%, cellulose 30.2%, lignin 11.9% and water 13.3%, Shafizadeh [11] described the two pathways of pyrolysis of cellulose and hemicellulose. The random nature of

hemicellulose which contains shorter polymeric chains suggest that its decomposition would yield primary products sooner than cellulose. Simmons and Lee [12] found two consecutive regimes corresponding to two different first order rates of formation of co in pyrolysis of wood. The first rate was related to the decomposition of hemicellulose whilst the second, was due to the decomposition of cellulose. It can be assumed from those observations that similar groups of reactions occur in the devolatilization of palm shell and fibre.

TABLE 2. Preliminary Results and Kinetic Parameters obtained from the devolatilization studies of palm shell and fibre

	Palm Shell (-0.500 + 0.353)			Palm Fibre		
Heating rate, °C min <sup>-1</sup>	25	40	80	25	40	80
Maximum rate of weight loss temperature, °C	307/382	315/390	335/400	305/370	312/377	325/380
Total devolatilization * (daf), %	71.1	70.9	71.7	77.6	77.4	78.0
Char * (daf), %	28.9	29.1	28.3	22.4	22.6	22.0
Activation Energy, E, KJmol <sup>-1</sup>						
Low	81.5	95.6	114.7	87.4	96.1	115.7
High	17.9	24.7	25.7	20.6	26.6	28.3
Frequency Factor, A, s <sup>-1</sup>						
High	6.01 × 10 <sup>4</sup>	4.94 × 10 <sup>5</sup>	1.16 × 10 <sup>7</sup>	2.36 × 10 <sup>5</sup>	9.44 × 10 <sup>5</sup>	2.44 × 10 <sup>7</sup>
Low	0.44	0.896	0.732	0.716	1.657	1.429

\*daf = dry and ash free

## CONCLUSION

The devolatilization of palm shell and fibre was studied by thermogravimetric analysis. Experiments were carried out at atmospheric pressure using nitrogen as the purge gas to a maximum temperature of 600°C. It was observed that the devolatilization process begins at around 200°C and is virtually complete at around 600°C. Two peaks were observed in the DTA curves of palm shell and fibre suggesting the existence of two different groups of reactions. The second peak coincides with that of the cellulose material investigated suggesting the same group of reactions. The first peak is assumed to be that of hemicellulose as implied by other workers.

There is a consistent lateral shift in the thermograms for both shell and fibre with respect to the heating rate. The yields of char and volatile matters for both fibre and shell are not affected by the heating rate. However, the yields of volatile matters from palm fibre are higher than that of the shell. Two different values of activation energies are obtained reflecting the two different groups of reactions. The low value activation energy is related to the first peak and the high value activation energy, which is approximately four times the low value, is related to the second peak. The activation energies were found to increase with increasing heating rates.

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