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PYROLYSIS OF RUBBERWOOD - A LABORATORY STUDY

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TAN, A.G. 1988. Pyrolysis of rubberwood - a laboratory study. The thermal degradation or pyrolysis of rubberwood in an inert environment was studied by monitoring the weight of its sample heated at 5.5° *C min*$^{-1}$ and analysing the decomposition products collected. The weight loss of the sample was gradual from 150° *C* to 280° *C*, fairly rapid from 280° *C* to 330° *C*, rapid from 330° *C* to 370° *C* and gradual again above 370° *C*. More than 70% of the sample's weight loss occurred between 280° *C* and 370° *C*.

The decomposition products collected up to a temperature of 550° *C*, when most of pyrolysis reactions have been completed, consisted of 57% condensate, 27% char and 16% gases, based on over-dried wood. The gaseous fraction was composed of around 55% carbon dioxide, 32% carbon monoxide and 13% methane, on a volume basis. Most of the volatile products were released between 280° *C* and 400° *C*. The condensate contained water, tar, acetic acid, methanol and other compounds.

Key words: Rubberwood - pyrolysis - decomposition - condensate - gases - volatile degradation products.

Introduction

Rubber (*Hevea brasiliensis*) is the main plantation crop of Malaysia, and it occupies around 2.0 million *ha*. The economic life span of the rubber trees is normally between 25 to 30 years, at the end of which they are felled to make way for replanting. In the 1970's, the wood of the rubber trees was mainly used for fuel, charcoal making and the production of chips for papermaking in Japan (Anonymous 1974). Today, a sizeable proportion of the rubberwood logs is channelled into sawn timber production for furniture manufacture.

The unused logs, together with the branchwood, are used as fuel, for charcoal production and for a variety of other applications, including particleboard manufacture. Interest has also been expressed in recovering the volatile degradation products from the wood for use as industrial chemicals. Preliminary work on this aspect had been carried out at the Rubber Research Institute Malaysia (RRIM) (Harris 1979). Further investigations on a larger scale are being planned.

In the exploitation of rubberwood as a source of charcoal and organic chemicals, it will be useful if the thermal degradation behaviour of the wood is clearly understood. Thus, a laboratory study was carried out in which the thermal decomposition or pyrolysis of rubberwood in an inert environment was examined and the resultant products analysed. The weight changes in the course of pyrolysis of the sample were also monitored. The results obtained are presented in this paper.

Materials and methods

Apparatus

The apparatus used consists of a reactor and an electrically heated furnace. The reactor is made up of three components, namely a pair of reaction tubes connected to a common gas coil, a stainless steel block serving as a heat sink and stand (Figure 1). Inside each tube is a circular piece of 13 *mm* thick ceramic fibre ('Kaowool') which serves as the gas distributor. It is supported by a stainless steel frame placed at the bottom of the tube. An orifice plug inserted at the entrance of each tube ensures that the gas flow rates in both the tubes are uniform. The reactor, weighing 31 *kg*, is placed inside the furnace with 66 *mm* of each reaction tube protruding out of the lid to facilitate collection of the volatile products. It could be bolted to the furnace lid and lifted out of the furnace at the end of each run for fan cooling.

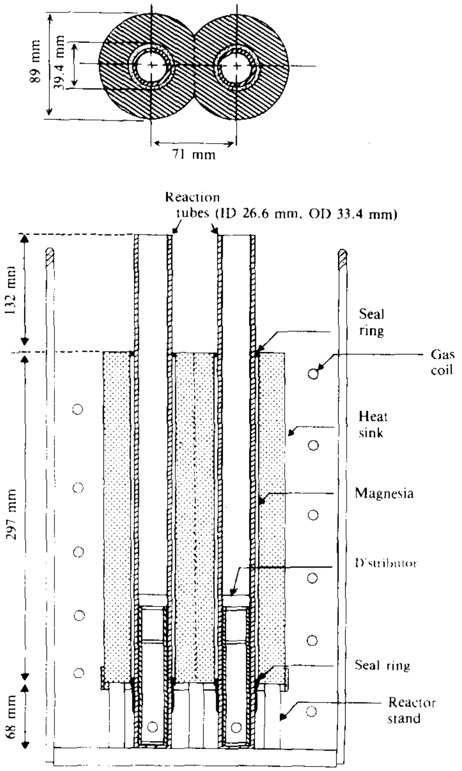

Figure 1. Schematic representation of reactor

Material

The rubberwood used was obtained from the Experiment Station of RRIM at Sungei Buloh, Peninsular Malaysia. A disc of thickness 50 *mm* and diameter 234 *mm* was extracted from the trunk of an old Tjir 1 tree and oven-dried. Rubberwood is a hardwood with an oven-dried density of around 600 $kg\,m^{-3}$. The elemental composition of the test samples was as follow : C 49%, O 44%, H 6% and ash 1%, on a dry weight basis.

Collection and analysis of pyrolysis products

The oven-dried test sample was placed in a stainless steel container (with a porous base) which was then lowered down with one of the tubes onto the gas distributor. The tube containing the sample is the sample tube while the other is the reference tube. Following this, the collecting device was set up, as illustrated in Figure 2. Nitrogen of 99.995% purity from a gas cylinder was passed through both the tubes with a combined flow rate of 0.4 min^{-1}. The reactor was heated at a constant rate of 5.5°*C* min^{-1}. Also heated was the connecting head joining the sample tube and the first collecting flask to prevent condensation of the heavier volatile fractions inside it. A chromel/alumel thermocouple of diameter 1 *mm* and length 700 *mm*, inserted in the reference tube, measured the reactor temperature which was continuously recorded on a chart recorder. The organic compounds and water were condensed in the two flasks while the gases were collected in the polythene bag. The experiment was stopped at around 550°*C* after most of the pyrolysis reactions had been completed. A run usually took between 1.5 - 2 *h* to complete.

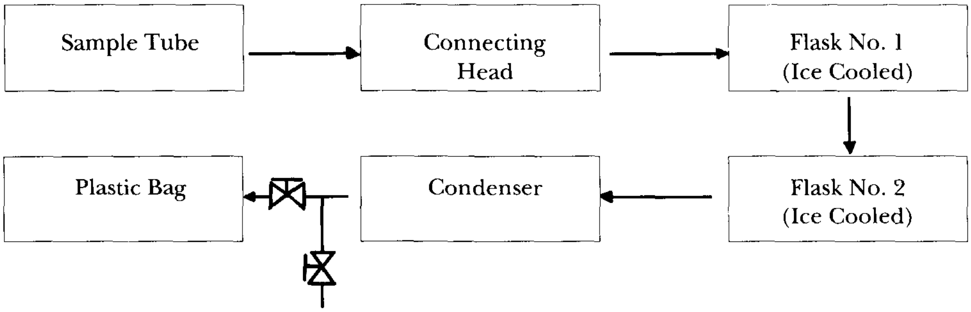

Figure 2. Block diagram of collecting device

After the reactor had cooled down sufficiently, the yields of the different pyrolysis products were determined, by direct weighing in the case of the condensate and char and with the aid of a gas meter and gas-liquid chromatography in the case of the gases. Carbon dioxide and methane were analysed using a Porapak Q column of length 2 *m* while a molecular sieve column (10% 5A and 90% 13X) of length 6 *m* was used in the analysis of carbon monoxide and nitrogen.

The condensate was analysed qualitatively using Nuclear Magnetic Resonance (NMR) spectroscopy. Two types of spectrometers, a Varian T-60 proton NMR and a Varian FT-80A carbon-13 NMR were used.

Thermogravimetry

The experimental setup for thermogravimetric analysis is shown in Figure 3. The sample holder consists of a stainless steel basket of 16 *mm* diameter and depth fabricated from 100-mesh screen. It is suspended at the end of a long wire, the other end of which is hooked onto the bottom of a digital balance (Mettler PE 360) which read up to three decimal places. After the test sample has been loaded, nitrogen is passed through the two tubes with a combined flow rate of 0.8 $l\ min^{-1}$. The reactor is then heated at around 5.5°*C* min^{-1}, as in the earlier experiments. Readings from the balance were recorded from the time the test sample began to lose weight, at intervals varying from 1 *min* (at the height of pyrolysis) to 5 *min*, until the rate of weight loss was almost constant, which came about to above 500°*C*. The actual heating rate was determined from the temperature curve traced on a chart recorder, after which the TG curve was plotted as a function of the reference temperature.

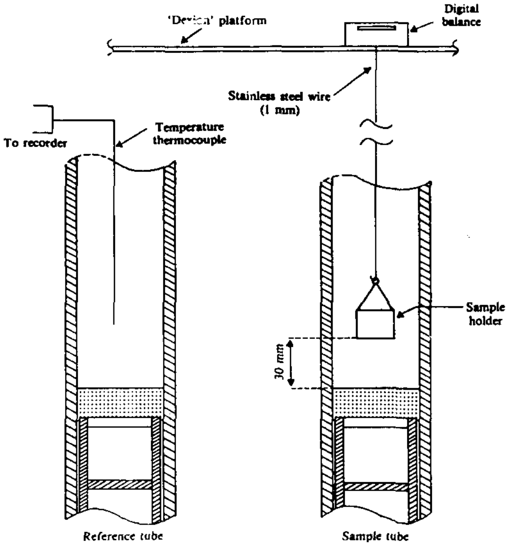

Figure 3. Experimental set-up for TG analysis

Results and discussion

Yields of pyrolysis products

The yields of the solid, liquid and gaseous pyrolysis products in four of the runs involving different particle sizes are presented in Table 1. It is noted that there was very little difference in the yield of each product between the runs, except that of the gases which was slightly higher in Run 3 than in the other three runs. The largest component was the condensate or liquid fraction which amounted to slightly over half the weight of the sample. The char yield was around 25% while that of the gases around 15%, on a weight basis. The product yields of Run 4 were close to those of the other three runs, although its final bed temperature was much higher. In all these runs, there was a small loss of material since the recovery rate ranged from only 92% to 95%. Assuming that the loss of each component was on a pro rata basis, the adjusted yields of the various products based on 100% recovery are as follows : condensate 57%, char 27% and gases 16%. In comparison, the pyrolysis product yields of two temperate hardwoods, as reported by Wenzl (1970), are as follows : (1) beechwood - condensate 49%, char 35% and gases 16% and (2) birchwood - condensate 54%, char 32% and gases 14%. The char yield of rubberwood is thus lower than those of beech and birch but there is very little difference in the amounts of gases produced by the three wood species. The variation in the pyrolysis product yields of different wood species is attributed to a difference in their chemical compositions.

Table 1. Yields of pyrolysis products

Run	Particle	Sample	% by weight			
No.	size	size (*g*)	Condensate	Char	Gases	Total
1	-18+36 mesh	5.4	53.40	25.49	14.68	93.57
2	-10+18 mesh	5.4	52.11	25.27	15.01	92.39
3	19 *mm* diam. pieces	8.3	52.21	25.86	17.25	95.32
4*	-18+36 mesh	5.5	53.89	24.62	14.38	92.89

* Experiment stopped at 635°*C* instead of 550°*C*.

The heating rate has an effect on the relative proportions of the pyrolysis products produced (Shafizadeh & DeGroot 1977). A study on this aspect for the test material could not be carried out due to the rather large thermal capacity of the reactor ($20\,kJ\,K^{-1}$) which limits the heating rate to a maximum of $7°C\ min^{-1}$. However, an illustration of this effect was carried out using flash pyrolysis in which the reactor was heated to and maintained at 530°*C* before a sample was lowered down the sample tube. Due to the high heating rate, the sample was completely pyrolysed within minutes. The char yield (20.8%) was appreciably lower than that obtained from pyrolysis using a heating rate of $5.5°C\ min^{-1}$ (27.0%). It can, therefore, be inferred that a high heating rate promotes the formation of the volatile products.

Yields of evolved gases

The yields of the various gases evolved were fairly consistent in the four runs (Table 2). Carbon dioxide was the biggest component (10%), followed by carbon monoxide (4%) and methane (1%). The average composition of the gaseous fraction, on a volume basis, was as follows: carbon dioxide 55%, carbon monoxide 32% and methane 13%. Hydrogen was detected only towards the end of each run but its yield was negligible.

Table 2. Yields of pyrolysis gases

Run	Yield (% of sample weight)			
No.	CO_2	CO	CH_4	Total
1	10.19	3.60	0.89	14.68
2	10.56	3.58	0.88	15.01
3	11.56	4.77	0.93	17.25
4	9.73	3.56	1.09	14.38

Two additional runs were conducted in which the evolution of the gases was monitored. The wood samples used were (1) -10 + 18 mesh particles of sample size 5.5 *g* (Run 5) and (2) 19 *mm* diameter pieces of sample size 9.3 *g* (Run 6). The gas samples were drawn out from the rubber hose connecting the condenser and the polythene bag. Analyses of carbon dioxide and methane were performed during the run, at approximately 5 *min* intervals while that of carbon monoxide was carried out after the run had been completed from samples stored in gas sampling tubes due to its long retention time (around 30 *min*). To a large extent, the evolution patterns of the various gases were similar in the two runs (Figures 4 & 5). Carbon dioxide was the first of the gases to be released, at around 170° *C*. Its concentration increased with increasing temperature, reaching a peak between 350° *C* and 370° *C*. After dropping sharply from the peak, it began to tail off at about 400° *C*. The evolution of carbon monoxide followed a similar pattern, except that its concentration was lower. Methane was liberated at higher temperatures, from around 320° *C*. Its level increased steadily and reached a peak around 430° *C*. It then dropped gradually and began to level off at 470° *C*. Above 520° *C*, the yield of methane exceeded that of carbon dioxide, on a volume basis. This explains why the yield of methane in Run 4, which had a higher final bed temperature, was greater than in the other three runs.

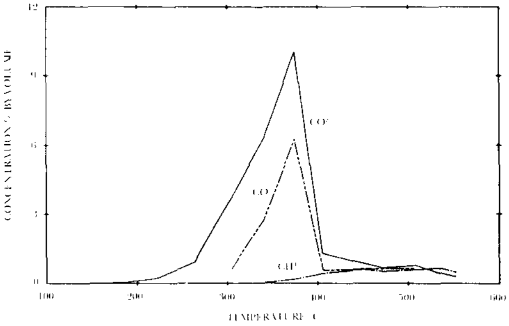

Figure 4. Concentrations of evolved gases in the gas stream - Run 5

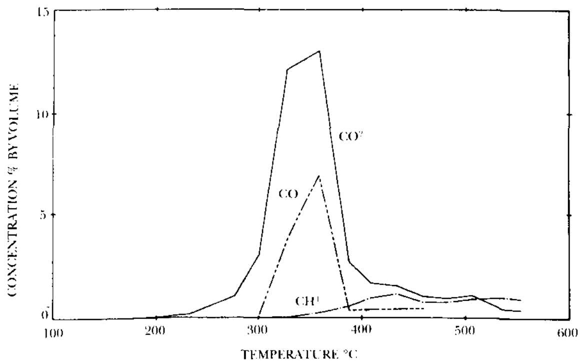

Figure 5. Concentrations of evolved gases in the gas stream - Run 6

Another four runs were carried out in which the temperature range within which the volatiles were collected was noted. The bulk of the volatiles was released between 280° *C* and 420° *C*, as in the case of carbon dioxide and carbon monoxide (Table 3). It thus appears that most of the decomposition reactions took place within this temperature range, being most vigorous around 360° *C*. It was observed that the condensate was light brown in colour and free flowing initially but turned darker and more viscous with increasing temperature.

Table 3. Temperature range within which the volatiles were released

Run No.	Particle size	Sample size (*g*)	Temperature (°*C*)	
			First drop collected	Last drop collected
7	-72+150 mesh	6.1	278	393
8	-36+72 mesh	6.3	293	403
9	-10+18 mesh	5.6	287	393
10	19 *mm* diameter pieces	7.3	281	404

NMR spectra of liquid fractions

The proton NMR spectra of the condensate were similar, and included those of water (δ = 5.2 ppm), acetic acid (δ = 2.0 ppm) and methanol (δ = 3.3 ppm) and a number of unidentified minor compounds. The carbon-13 NMR spectrum of the condensate contained numerous signals, they are attributed to acetic acid and methanol, phenols, their corresponding aromatic ring carbons, and carbohydrate-like structures. The spectra of two other fractions examined, from Runs 4 and 8, were similar to that of this run.

The proportions of water and the other chemical compounds in the condensate were not determined. However, figures for other hardwoods are available in the literature. For example, the dry distillation of beechwood produced 44.9% by weight of condensate, comprising 25.4% water, 6.7% acetic acid, 10.5% tar and 2.3% methanol and other minor chemicals (Wenzl 1970).

Harris (1979) has carried out some studies on destructive distillation of rubberwood using an iron retort. From these studies, the following product yields were reported: charcoal 28%, acetic acid equivalent 5%, tar 7% and spirit 1.2%.

Thermogravemetric curves

The TG curves of (i) -36+72 mesh particles of sample size 0.6 *g* and (ii) 5 *mm* diameter pieces of sample size 1 *g* are shown in Figure 6. Both the samples began to lose weight at around 150° *C*. The weight loss was gradual up to 280° *C*, rapid from 280° *C* to 330° *C*, very rapid from 330° *C* to 370° *C* and gradual again above 370° *C*. More than 70% of the total weight loss of each sample occurred between 280° *C* and 370° *C*, the same temperature range within which most of the volatiles and gases were liberated. The weight loss patterns of the two samples were fairly similar, and the small gap between the two curves above 370° *C* indicates that there was a slight difference in their char yields.

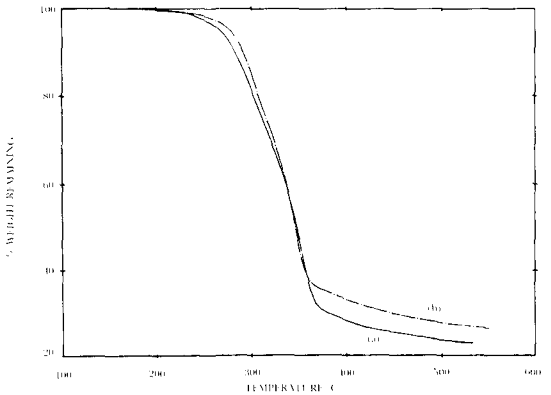

Figure 6. TG curves in 2 of (a) -36 +72 mesh particles and (b) 5 *mm* diameter pieces

TG curves were obtained for the individual wood components with the aim of gaining an insight on their relative thermal stabilities. In general, hardwoods contain around 40% cellulose, 33% hemicelluloses, 20% lignin and 7% extractives, on a weight basis (Shafidah & DeGroot 1976). Lignin and the water-solubles were extracted from rubberwood following standard procedures while filter paper was used as the source of cellulose. As the preparation of lignin involved the use of concentrate sulphuric acid to dissolve the polysacchyarides, the resultant product was referred to as acid lignin. The TG curves of the individual wood constituents are presented in Figure 7, including that of xylan, the main hemicellulose component, obtained by Shafizadeh and DeGroot (1976). It is seen that the water-solubles were the least stable of the four wood constituents, beginning to lose weight at around 120° *C*, compared with 180° *C* for acid lignin, 200° *C* for xylan and 260°*C* for cellulose. Most of the weight loss occurred between 240°*C* and 310°*C* for the water-solubles, between 250°*C* and 320°*C* for xylan, between 310°*C* and 390°*C* for cellulose and between 320°*C* and 460°*C* for acid lignin. This means that, overall, acid lignin is the most stable thermally of the four wood constituents, followed by cellulose and then by the other two components. The results obtained that the pyrolysis of rubeerwood involves mainly the extractives and the hemicelluloses below 300°*C* and cellulose and lignin above 300°*C*. It seems clear that the most active region, that is between 330°*C* and 370°*C*, is attributed to degradation of cellulose.

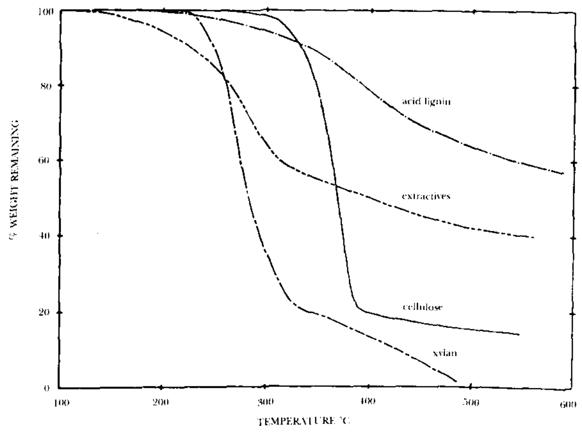

Figure 7. TG curves in N_2 of individual wood components

The char yield of the individual wood components increased in the order: xylan, cellulose, water-solubles and acid lignin. At 500°*C*, for example, the amounts of char produced by the various components were as follows: acid lignin 64%, water-solubles 42%, cellulose 15% and xylan, negligible. The char yield of rubberwood was between those of cellulose and the water-solubles. Lignin and the extractives, thus, contribute more to char formation than cellulose and the hemicelluloses, percentage wise. Conversely, cellulose and the hemicelluloses produce more volatiles than the other two components. As the chemical composition of wood varies from species to species, it is natural that there is a variation in the composition of their pyrolysis products. It is, perhaps, useful to mention here that the volatiles are the products which give rise to flaming combustion in wood, as opposed to glowing combustion by the char.

Heat changes during pyrolysis

The heat changes taking place in the course of pyrolysis of rubberwood in an inert atmosphere have been investigated using Differential Thermal Analysis (DTA) (Tan & Stott 1987). Some of the findings of this investigation are reproduced here to provide a more complete picture of the subject being discussed.

The DTA experiments were carried out in the same apparatus as the one used in the present study.

Figure 8 shows the DTA curves of some rubberwood samples resulting from runs using a sample size of 3 *g*, a combined nitrogen flow rate of 0.8 $l\ min^{-1}$ and a heating rate of 5.5°$C\ min^{-1}$. The DTA curves of the <150 mesh, -36+72 mesh and -10+18 mesh particles were fairly similar in shape, with each containing a number of individual or overlapping reaction peaks. These peaks included a weak endotherm lying between 130°*C* and 180°*C* (A), part of an endotherm beginning at around 155°*C* (B), an exotherm peaking at 320°*C* (C), an endotherm peaking at 360°*C* (D), a strong exotherm peaking at 400°*C* (E) and a weak endotherm at around 500°*C* (F). Further experiments carried out on the individual wood components showed that Exotherm C is linked mainly to the hemicelluloses and the extractives, Endotherm D to cellulose and Exotherm E to lignin. The DTA curves of the 5 *mm* and 10 *mm* diameter pieces (length 14 *mm*) contained an extra exotherm between 340 and 380°*C* (G). In addition, Exotherm C was relatively large in size while Endotherm B was almost non-existent in these curves. In increasing the particle size from 5 to 10 *mm* in diameter, Exotherm G grew in size, apparently at the expense of Exotherm E. From these results, it is evident that the thermal behaviour of rubberwood is dependent on particle size, which has an influence on the heat transfer to the interior and escape of volatiles to the exterior of the wood particles. The exotherms in the DTA curves of the 5 and 10 *mm* diameter test pieces were more prominent than the endotherms, indicating that the thermal degradation of these wood pieces has a nett exothermic effect.

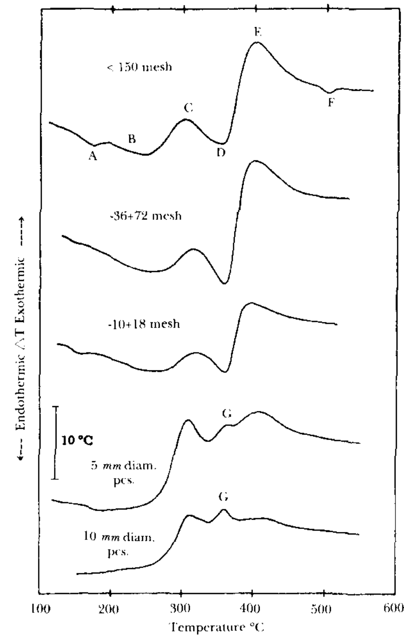

Figure 8. DTA curves in N_2 of rubberwood of different particle sizes

Conclusion

The pyrolysis of rubberwood in an inert atmosphere, as studied by thermogravimetric analysis, begins at around 150° *C* and is most vigorous between 330° *C* and 370° *C*, which corresponds to degradation of cellulose. Above 370° *C*, the rate of weight loss is much reduced as most of the decomposition reactions have been completed.

The condensate is the biggest component of the pyrolysis products, comprising slightly over half the weight of the sample. The gaseous fraction, with a yield of around 16%, consists mainly of carbon dioxide with carbon monoxide and methane as the minor components. A large proportion of the volatiles and gases is released between 280° *C* and 400° *C*, indicating that most of the decomposition reactions occur within this temperature range.

A number of reactions, both exothermic and endothermic, take place in the pyrolysis of rubberwood. As the particle size increased, the exothermic reactions become more dominant.

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