The Low Pressure Pyrolysis of Newsprint

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Synopsis

The isothermal pyrolysis of 100 mg samples of shredded newsprint, both untreated and 1% HCl washed, at pressures below 1 torr has been examined between 260°C and 340°C. Pyrolysis occurs via a rapid initial reaction followed by a slower degradation that can be modeled as first order in remaining newsprint. The effect of a 1% HCl wash pretreatment is to increase the fractional tar yield by 40%, to decrease the gas yield by an equivalent amount, and to increase the extent of initial reaction. Arrhenius parameters have been obtained for rate constants describing both the initial and the slower degradation reactions for both untreated and acid washed newsprint.

INTRODUCTION

A better understanding of the chemical reactions involved in the rapid thermal degradation of paper is important for the design of processes that convert waste material into valuable chemicals or fuels, as well as for improved measures of fire control. Metropolitan areas face a difficult waste disposal problem. Environmental regulations have restricted the incineration and ocean dumping of solid wastes, and costs for burial in landfills have escalated. Several pyrolysis processes have been proposed for turning urban waste into marketable products.[1-4] However, none of these has as yet proven both economically feasible and environmentally acceptable. We have undertaken a study of the pyrolysis of newsprint, the cellulosic material found in greatest quantity in urban waste to better define the factors controlling product yield. Such information will be useful for the improved design of commercial pyrolysis plants. It should also aid the development of superior methods to control newsprint's combustibility. This is important because milled newsprint is finding increasing use as building insulation.

Considerable research has been done on the pyrolysis of wood and of pure cellulose. Extensive reviews of earlier work have been published.[5-10] Most previous experimental studies of the pyrolysis of small samples of cellulosics have been performed using some type of TGA analysis. The shortcomings inherent to this technique include: uncertainties in temperature measurement, a general limitation to heating rates below 100°C/min, and difficulties in product recovery that usually limit the kinetic analysis to one based upon overall weight loss data.[5,10-13] The present work differs from most previous research in that the pyrolysis products have been monitored as a function of time. There are recent studies on cellulose[14] and wood[15] in which this was done, but we know of no similar work on newsprint or any other paper. Rogers and Ohlemiller[16] have examined the thermal degradation of milled newsprint using TGA and DSC

techniques in which only overall weight loss was used to describe the rate of re-action.

Pyrolysis products from any cellulosic material are conveniently grouped into three classes: char, tars, and gases. Char is a carbon-rich, nonvolatile residue. Tars are any of several high molecular weight products that are volatile at py-rolysis temperatures but condense onto any surface near room temperature. Gases include all lower molecular weight products, including water, that have readily measurable vapor pressures at room temperature. Any one of these three classes could be the most desirable product. Most commercial scale pyrolysis plants are designed to have only one class as the principal product with at least one of the other classes serving as a fuel source. For manufacture of carbon black, charcoal, or activated carbon, the char is of principal interest. Low molecular weight compounds are of primary importance when the goal is a low to medium heating value fuel gas. Finally, the tar fraction can be used to create fuel oil or chemical feedstocks. Because of the high value of these latter products, the tars have the greatest economical potential.

Principal factors determining the product mix are the temperature, the heating rate, the residence time at high temperature, the ambient atmosphere, and the nature and purity of the cellulosic substrate. The influence of these parameters can be interpreted in terms of a competition between two types of cellulose degradation reactions, ring scission and end-group depolymerization.[17-19] The ring scission reactions lead primarily to char and gases, while tars are the main products of the depolymerization reactions. At temperatures below about 300°C the ring scission reaction is favored over depolymerization. Higher heating rates cause temperatures favorable to depolymerization to be reached more quickly and, hence, give higher tar yields. Each of these two types of product formation reactions is preceded by reactions altering the substrate but causing only minor changes in weight. Ring scission is preceded by loss of water and creation of "anhydrocellulose"; end-group depolymerization is preceded by a degradation in molecular weight. Trace inorganic impurities are thought to catalyze the ring scission pathway. Dilute acid wash treatments have proven useful in raising the tar yield from several cellulosic materials.[20]

All high molecular weight depolymerization products may undergo secondary decomposition. Factors that reduce a tar molecule's residence time at high temperature, such as low pressure and small sample size, give enhanced tar yields.

This paper reports on a series of experiments carried out to quantify the effect of temperature on pyrolysis yields of newsprint under conditions of high heat-up rates and very low pressure, i.e., minimal secondary decomposition of tars. Experiments were performed on both newsprint that received a mild 1% HCl wash treatment and untreated substrate. The temperature range examined was 260–340°C, a region where heat of reaction effects are known to be small and tar formation rates are large.[14] A rapid initial decomposition was observed during sample heat-up. This was followed by a slower isothermal degradation. The isothermal data are consistent with a rate model involving decomposition through competing reaction channels which are first order in unreacted newsprint. The results are compared with similar experiments on pure cellulose[14] and on saw-dust.[15]

EXPERIMENTAL

The pyrolysis apparatus is modeled after that first used by Madorsky and co-workers at the National Bureau of Standards[21] and more recently by Bradbury et al.[14] The apparatus is sketched in Figure 1. It is a simple, highly reliable, and versatile setup that permits fractionation and recovery of the pyrolysis products and facilitates accurate temperature measurement. The reactions are carried out in a cylindrical quartz chamber approximately 13 cm long and 4 cm in diameter that is sealed between lengths of standard 4 cm diameter Pyrex tubing. The quartz cylinder is wrapped with a 300-W heating tape and insulating material. One end of the cylindrical quartz and Pyrex tubing leads to an isopropanol slush bath (−88°C) and liquid nitrogen (−196°C) cold trap in series with a mercury manometer, a McLeod gauge, and a mechanical vacuum pump. The other end of the cylindrical tubing has an inlet valve for bleeding nitrogen, a thermocouple lead wire, and room for housing a small aluminum boat away from the high temperature quartz chamber.

An aluminum boat, made by wrapping aluminum foil around a paper clip, is used to hold and transport the pyrolysis samples. Boat dimensions are 5.2 cm × 1.2 cm × 1.4 cm (1 × w × d) and the mass is 2 g. A chromel/alumel thermocouple is positioned in the center of the boat, with the tip lying a few millimeters above the boat's floor. Temperature is monitored using a strip chart recorder and a digital multimeter. The boat and attached thermocouple tip can be quickly moved into or out of the quartz chamber by means of a hand-held magnet.

The pyrolysis samples are newsprint obtained from a Sunday edition of *The New York Times* and treated in the following manner: the newsprint is first fed repeatedly through a "Secromat" Model 2 commercial paper shredder; next it is shaken through a 4-mesh (4.75-mm) screen; then it is dried in a 70°C oven
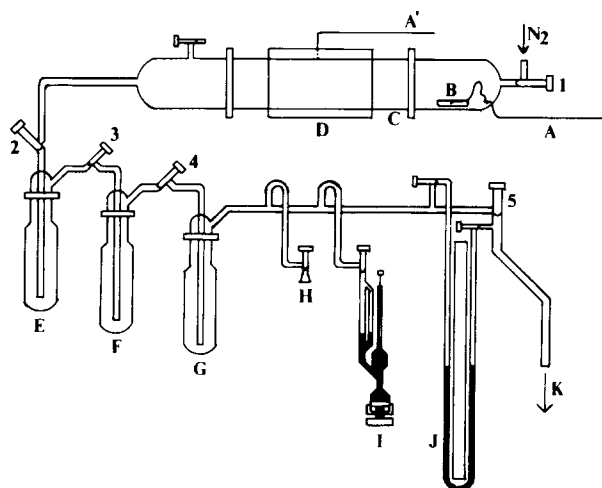

Fig. 1. Experimental apparatus: (A,A′) thermocouple wires; (B) sample boat; (C) Pyrex cylinder; (D) insulated, quartz pyrolysis zone; (E, F, G) cold traps; (H) sample port; (I) McLeod gauge; (J) manometer; (K) connection to vacuum pump; (1–5) PTFE valves.

and stored in a dessicator until used for pyrolysis. Prior to the above drying step, some paper is given an acid wash treatment by soaking in a 1% HCl solution for about 4 h, with occasional mild stirring, followed by repeated rinsing with distilled water until neutralized.

100-mg samples of moisture-free newsprint are weighed into an aluminum boat, filling it roughly halfway. Experiments are begun by placing a boat with sample and attached thermocouple in the pyrex arm of the reaction chamber, evacuating the entire apparatus to below 0.1 torr and heating the quartz section to a temperature slightly above that of a pyrolysis. Next, power to the heating tape is reduced, using a Powerstat, to that necessary for maintaining pyrolysis temperature, the vacuum pump is valved off, and the aluminum boat is brought to the center of the quartz chamber. Using this procedure, initial heat-up rates of at least 390°C/min are achieved and the pyrolysis temperature is reached within two minutes for temperatures over the range of 260–340°C (see Fig. 2 below).

During the pyrolysis, gases diffuse into the cold traps while tars diffuse only a short distance out of the pyrolysis zone before condensing on the glass wall. Formation of noncondensible gases causes a pressure increase of less than 1 torr.

After the boat has been in the pyrolysis chamber for a set period of time, it is quickly moved by a magnet into a cool arm of the apparatus, and the quartz section is allowed to cool. The cold traps are then sealed off from the pyrolysis chamber. After the traps are brought to room temperature, the pressure is measured with a McLeod gauge or mercury manometer.

After the pyrolysis chamber has cooled, the vacuum is broken, and the aluminum boat is carefully removed and weighed. Tars produced during the pyrolysis condense on the cool Pyrex arms surrounding the quartz chamber. These tars are recovered by rinsing the quartz-Pyrex tube with acetone, collecting the tar–acetone solution in a vial of known weight, and evaporating the acetone.

The ash content of newsprint is determined using ASTM Method D 3174-73, in which a crucible containing a sample of known weight is held at 700°C in air for a time sufficient to give a constant weight of residue.

The principal measured parameters are the pyrolysis temperature, the pyrolysis time, the weight of residue in the sample boat, and the weight of the product tars. The initial sample weight and the ash content of the newsprint are also known. Our following model for the rate of thermal degradation of the newsprint is based upon this information.

THEORY

Models used to describe the kinetics of cellulosic pyrolysis usually greatly simplify the set of consecutive and parallel reactions previously described. Our immediate goal is a simple model for the overall degradation of newsprint. To this end we will suppose the tar and char products are formed in independent reactions both of which are homogeneous and first order in remaining substrate.

The basic rate equations are thus

$$\frac{dW_N}{d\theta} = -k W_N \tag{1}$$

$$\frac{dW_t}{d\theta} = k_t W_N \tag{2}$$

$$\frac{dW_c}{d\theta} = k_c W_N \tag{3}$$

where W is weight, θ is time, the k are rate constants, and the subscripts N, t, and c refer to newsprint, tar, and char respectively. The subscripted k is the rate constant for overall degradation.

These equations may be integrated subject to the initial condition that when isothermal conditions are first achieved the amount of newsprint is W_N^0, the amount of tar formed during the heat-up period is W_t^0, etc. The weight of tar as a function of time is thus

$$W_t = W_N^0 \frac{k_t}{k} (1 - e^{-k\theta}) + W_t^0 \tag{4}$$

where zero time is that of attainment of isothermal conditions.

It is convenient to express this equation in the form

$$\frac{W_{t\infty} - W_t}{W_s} = \frac{W_N^0}{W_s} \frac{k_t}{k} e^{-k\theta} \tag{5}$$

where $W_{t\infty}$ is the weight of tar produced after "infinite" time and W_s is the initial weight of sample exclusive of ash. $W_{t\infty}$ is experimentally measured following pyrolyses of sufficient duration for the residue and tar weights to have become constant in time.

An equation similar to (5) can be developed for the weight of residue in the sample boat, R. This equation is

$$\frac{R - R_\infty}{W_s} = \frac{W_N^0}{W_s}\left(1 - \frac{k_c}{k}\right) e^{-k\theta} \tag{6}$$

where R is the sum of the weights of unreacted newsprint, char, and ash. The left-hand sides of both eqs. (5) and (6) are measurable quantities. Their natural logarithm plotted vs. time should be a straight line whose slope is the negative of the overall degradation rate constant. The intercepts of these plots are the zero time values of eqs. (5) and (6).

The weights of tar and residue at what is effectively infinite time can be used in conjunction with the zero-time values from eqs. (5) and (6) to give measures of the extent of the newsprint's nonisothermal or initial reaction:

$$\frac{W_t^0}{W_s} = \frac{W_{t\infty}}{W_s} - \frac{W_{t\infty} - W_t^0}{W_s} \tag{7}$$

$$\frac{R^0}{W_s} = \frac{R_\infty}{W_s} + \frac{R^0 - R_\infty}{W_s} \tag{8}$$

RESULTS

Representative heat-up curves for each of five pyrolysis temperatures we have
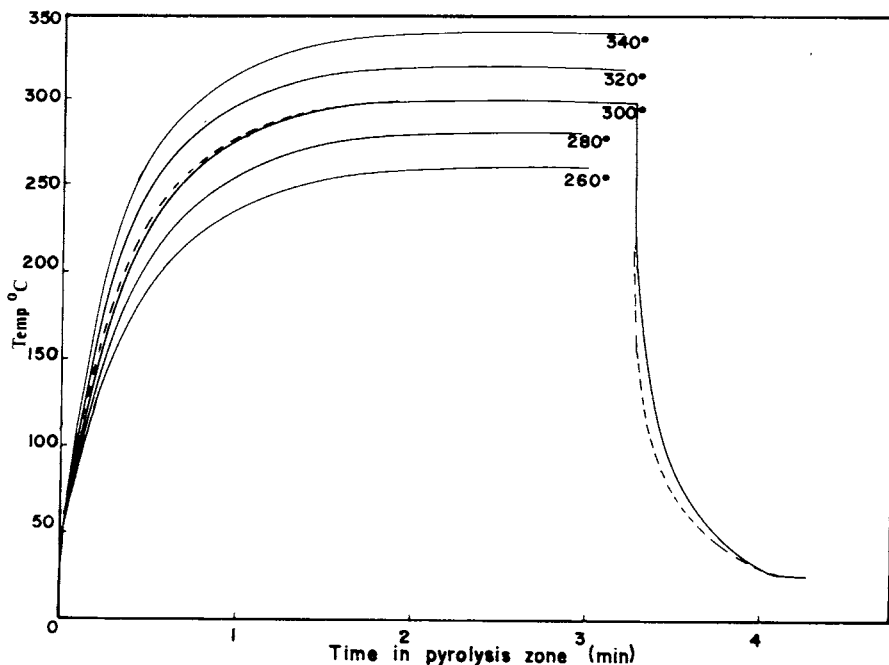
Fig. 2. Heating rate curves. The dashed line describes the heat-up and cooling of an empty sample boat. The final pyrolysis temperatures are shown.

examined are shown in Figure 2. Also shown for a temperature of 300°C is the rapid cooling of the sample when withdrawn from the quartz pyrolysis zone and the corresponding heat-up and cooling curve for an empty boat with the ther-
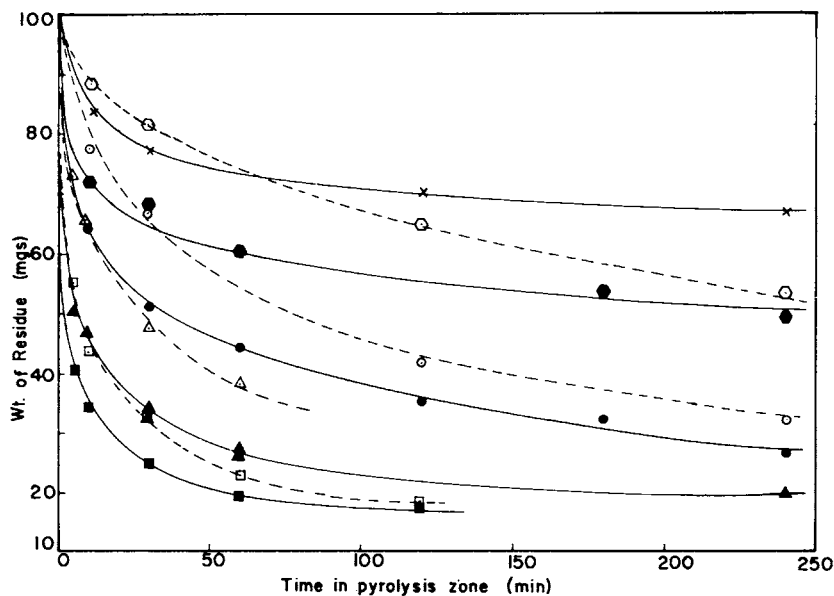

Fig. 3. Weight of sample residue vs. time in the pyrolysis chamber. The dashed lines and open figures are for untreated newsprint; the solid lines and figures are for 1% HCl washed newsprint. Pyrolysis temperatures are 260°C (X), 280°C (⊙), 300°C (O), 320°C (△), and 340°C (□).
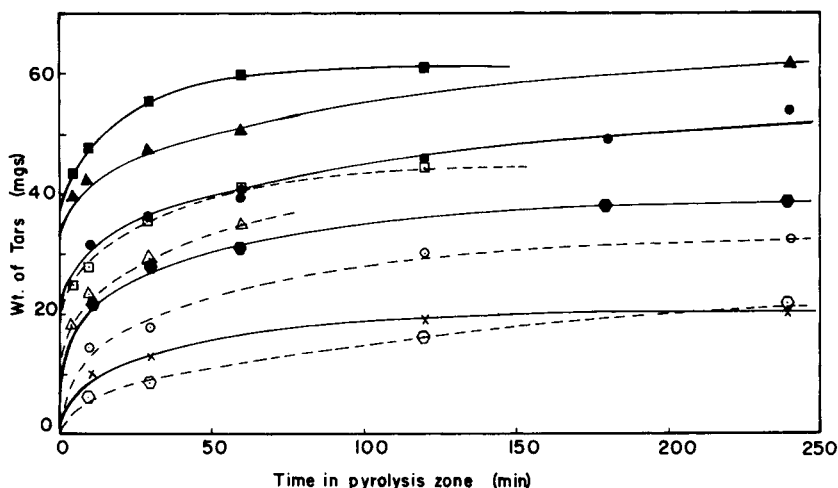
Fig. 4. Weight of tar products vs. time in the pyrolysis chamber. The symbols and line features are identical to those in Figure 3.

mocouple tip held against the boat's floor. All of the curves are highly reproducible for pyrolyses at any given temperature. In every case the final pyrolysis temperature is reached in just under two minutes time. Hence, zero time in eqs. (1)–(8) is taken as 2 min after the boat enters the pyrolysis chamber.

Figure 3 shows plots of the weight of residue vs. time for all temperatures and both acid washed and untreated newsprint. The solid lines are smooth curves drawn through the data for acid washed newsprint (filled figures) and the dashed lines pass through the data on unwashed newsprint (open figures). The amount of residue at infinite time, i.e., the char yield, falls with increasing temperature. Also, the initial rate of weight loss is greater at higher temperatures and with acid wash treatment.

Figure 4 shows the variation in weight of tars with time for different temperatures with both acid-washed and unwashed newsprint. More tar is formed at higher temperature and with acid wash treatment.

The duration of experiments taken as being of effectively infinite time are listed in Table I as θ_∞. The fractional yields of tar, char, and gases in such experiments are also listed for both untreated and acid washed newsprint. The gas yields were calculated from the measured tar and char yields by mass balance. It can be seen that, as the pyrolysis temperature increases, the tar yields increase,

TABLE I
Infinite Time Fractional Product Yields

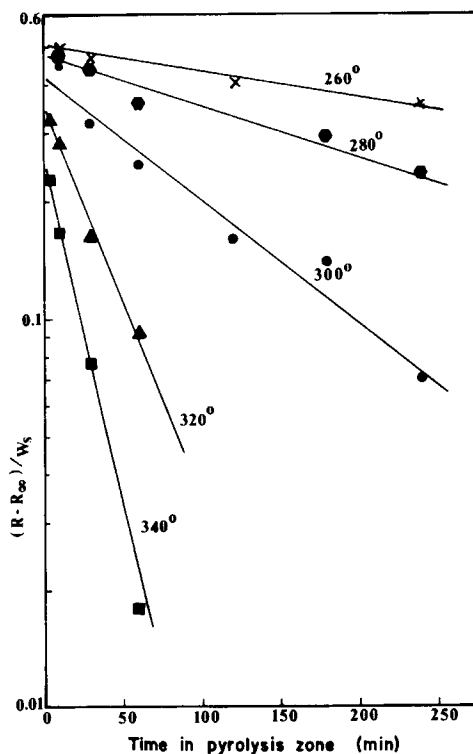| T (°C)	θ_∞ (h)	Untreated newsprint			Acid-washed newsprint		
		$W_{t\infty}/W_s$	$W_{c\infty}/W_s$	$W_{g\infty}W_s$	$W_{t\infty}/W_s$	$W_{c\infty}/W_s$	$W_{g\infty}/W_s$
260	80				0.45	0.31	0.24
280	48	0.37	0.24	0.39	0.54	0.25	0.21
300	24	0.43	0.22	0.35	0.58	0.19	0.23
320	6	0.43	0.20	0.37	0.60	0.18	0.22
340	2	0.44	0.18	0.38	0.61	0.17	0.22
Ash content		0.6 wt %			0.2 wt %		

Fig. 5. Semilogarithmic plot of $(R - R_\infty)/W_s$ vs. time for acid washed newsprint at the indicated pyrolysis temperatures (°C).

the char yields decrease, and the gas yield remains approximately constant. For temperatures above 300°C the yields of all three products show only minor variation with temperature. Comparison of the untreated and acid-washed newsprint product yields shows that the acid pretreatment increases the fractional tar yield by about 40%, causes a slight decrease in char yield, and substantially reduces the gas production. The ash contents of the untreated and acid washed newsprint are given at the bottom of Table I and show the acid pretreatment reduces the level of inorganic impurities by a factor of three.

Figures 5 and 6 give semilogarithmic plots of ln $[(W_t - W_{t\infty})/W_s]$ and ln $(R - R_\infty)/W_s]$ vs. time for acid washed newsprint pyrolyzed at five different temperatures. These plots are suggested by eqs. (5) and (6). While occasional scatter is present, the linearity of the data is apparent. The lowest correlation coefficient for any temperature is 0.95. The solid lines represent least-squares linear fits to the data.

The untreated newsprint pyrolyses also show linearity in plots similar to Figures 5 and 6. Table II summarizes the results of linear regression analyses on both the untreated and acid-washed newsprint. The negative of the slopes of the linear data fits represents the rate constant for the overall degradation of newsprint. The intercept from Figure 5 is $(W_{t\infty} - W_t)/W_s$ at a time equal to 2 min in the pyrolysis chamber which is zero time in eqs. (5) and (6). The
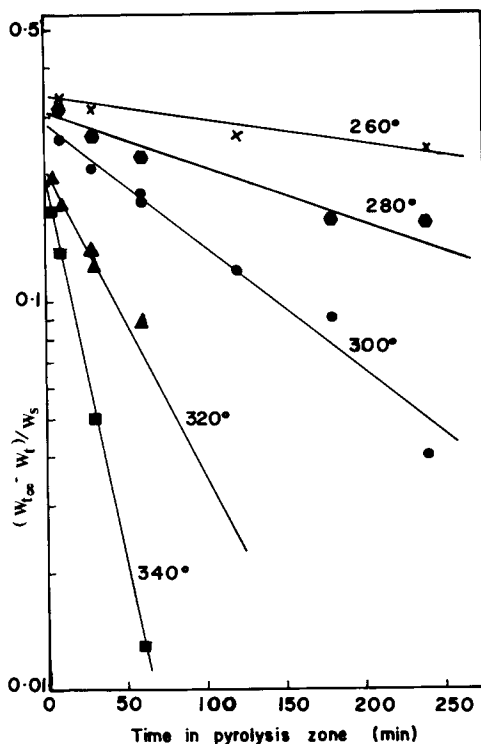
Fig. 6. Semilogarithmic plot of $(W_{t\infty} - W_t)/W_s$ vs. time for acid washed newsprint at the indicated pyrolysis temperatuares (°C).

intercept of the residue data, as plotted in Figure 6, is also included in Table II.

Notice from Table II that the slope based upon the tar data is always within 7% of the slope obtained from the weight of residue data. The consistency of the slopes between Figures 5 and 6 supports both the experimental procedure and the assumption of first-order, homogeneous decomposition. In addition, comparison of the untreated and acid washed newsprint results shows that acid washing causes the overall rate constant to become more sensitive to temperature.

TABLE II
Linear Regression Results

Pyrolysis temp (°C)	Untreated newsprint				Acid-washed newsprint			
	Tar data		Residue data		Tar data		Residue data	
	−Slope (min⁻¹)	Intercept	−Slope (min⁻¹)	Intercept	−Slope (min⁻¹)	Intercept	−Slope (min⁻¹)	Intercept
260					0.00136	0.329	0.00146	0.493
280	0.00308	0.322	0.00338	0.634	0.00296	0.301	0.00299	0.487
300	0.00793	0.306	0.00757	0.543	0.00755	0.283	0.00722	0.418
320	0.0188	0.250	0.0187	0.520	0.0225	0.226	0.0218	0.323
340	0.0328	0.201	0.0351	0.383	0.0469	0.194	0.0454	0.257

TABLE III
Initial Decomposition

T (°C)	Untreated newsprint		Acid-washed newsprint	
	$\overline{W_t^0/W_s}$	R^0/W_s	$\overline{W_t^0/W_s}$	R^0/W_s
260			0.12	0.81
280	0.05	0.88	0.24	0.70
300	0.12	0.77	0.30	0.61
320	0.18	0.73	0.38	0.51
340	0.24	0.57	0.42	0.43

Arrhenius parameters for the isothermal decomposition of acid washed and untreated newsprint were obtained by a least-squares analysis of ln k vs. inverse temperature data. The derived Arrhenius expressions for the overall rate constants are:

$$k = 1.1 \times 10^9 \ (\text{min}^{-1}) \ \exp(-122 \ \text{kJ/mol} /RT) \quad \text{for acid-washed newsprint}$$

$$k = 1.3 \times 10^8 \ (\text{min}^{-1}) \ \exp(-112 \ \text{kJ/mol} /RT) \quad \text{for untreated newsprint}$$

The extent of the initial reaction, that occurring prior to the isothermal degradation described by eqs. (1)–(6), may be estimated from the 2-min time values of Figures 4 and 5. It is only after 2 min of pyrolysis that isothermal conditions are achieved. Equations(7) and (8) subtract from the infinite time fractional yields those weight changes due to isothermal degradation. These differences, which we call the extent of initial reaction, are listed in Table III. They represent the amount of reaction that would occur in the 2-min heat-up period if eqs. (5) and (6) become valid immediately after attaining the final pyrolysis temperature.

The largest measured isothermal rate constant predicts only a 9% conversion of newsprint during a 2-min time period. From Table III, the smallest weight loss during the initial reaction, $1 - R^0/W_s$, was 12%. This illustrates that the initial degradation is distinct from the subsequent isothermal reaction. The thermal degradation of newsprint takes place in two steps: a rapid initial decomposition followed by a slower isothermal reaction.

The significance of the initial reaction can be seen from Table IV. This lists the amount of sample weight loss and tar formation during the early non-isothermal pyrolysis as a fraction of the ultimate, "infinite time" weight loss and tar formation. The initial reaction accounts for a much greater percentage of the total degradation reactions as temperature increases and with acid-wash pretreatment. Recall the initial reaction occurs over a time period of close to

TABLE IV
The Ratio of Initial Reaction to Total Reaction

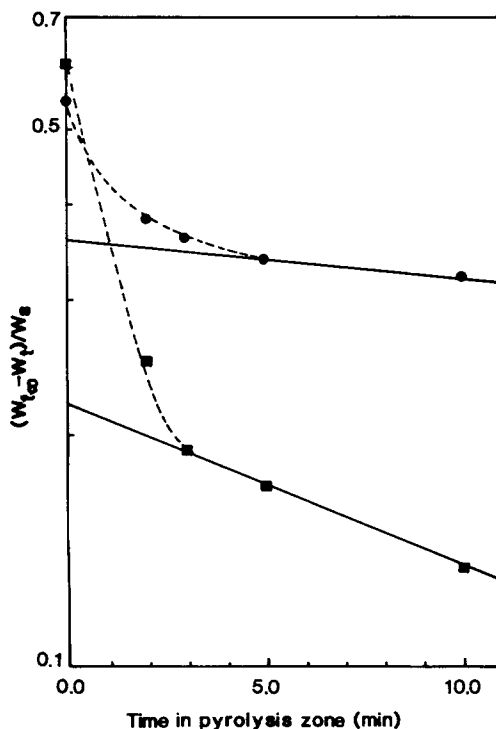| T/(°C)	Untreated newsprint		Acid-washed newsprint	
	$\overline{W_t^0/W_{t\infty}}$	$1 - R^0/W_s/1 - R_\infty/W_s$	$\overline{W_t^0/W_{t\infty}}$	$1 - R^0/W_s/1 - R_\infty/W_s$
260			0.27	0.28
280	0.14	0.16	0.44	0.35
300	0.28	0.29	0.52	0.48
320	0.42	0.34	0.63	0.60
340	0.55	0.52	0.69	0.69

Fig. 7. Semilogarithmic plot of $(W_{t\infty} - W_t)/W_s$ vs. time for acid washed newsprint at short pyrolysis times. The solid lines are eq. (5) and the dashed lines are smooth curves drawn through the data, ($\bullet$) 280°C and ($\blacksquare$) 340°C.

2 min and the isothermal reaction takes place over several hours. Table IV shows that at 300°C with acid-washed newprint, the first half of the pyrolysis occurs within a few minutes while the second half requires some 20 h. Figure 7 presents tar formation data from short-time experiments (less than 10 min) at 280°C and 340°C with acid-washed newsprint. The solid lines are plots of eq. (5) describing isothermal, first-order decomposition. They are extensions of the solid lines shown in Figure 6. The dashed lines are smooth curves drawn through experimental data obtained from 2- and 3-min pyrolyses. These data show the rapid initial reaction is essentially over within 3 min of the sample's entry to the pyrolysis chamber.

The temperature dependence of the initial reaction can be modeled in terms of a zero-order rate constant, k_0, defined by

$$k_0 = \frac{1 - R^0/W_s}{\theta_i} \qquad (9)$$

where θ_i is some time characteristic of the initial reaction period. We have taken θ_i as 2 min since this is the time necessary to achieve isothermal conditions as shown in Figure 2, and is a reasonable estimate of the time period for initial reaction. (We infer from Fig. 7 that the initial reaction is finished within three minutes and from Fig. 2 that it is initiated only after 0.5–1 min, the time required to achieve 250°C.) Provided θ_i is insensitive to temperature, the values of θ_i
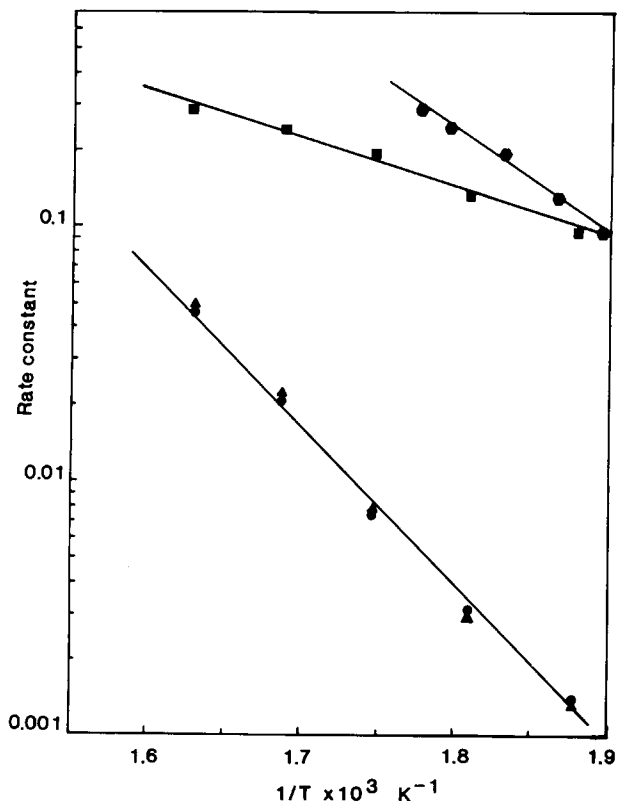
Fig. 8. Arrhenius plots for the decomposition rate constants of 1% HCl washed newsprint at 260–340°C, (●) k from residue data, (▲) k from tar data, (■) k_0 based on the final pyrolysis temperatures, and (⬤) k_0 based upon the time average temperature above 250°C.

affects only the deduced Arrhenius preexponential factors and will not change the derived activation energies.

We have considered two possible choices for the temperature that would characterize the initial reaction. These choices are the final pyrolysis temperature and the time average temperature between 250°C and the final pyrolysis temperature. We believe these choices represent different extreme values for the actual temperature describing the initial reaction.

Arrhenius parameters have been determined by linear least squares analyses of ln k_0 vs. inverse temperature data. When the temperature is taken as the final pyrolysis temperature the Arrhenius expressions for the rate constants are:

$k_0 = 6.0 \times 10^2$ (min^{-1}) exp(-38.7 kJ/mol $/RT$)   for acid-washed newsprint

$k_0 = 1.4 \times 10^4$ (min^{-1}) exp(-56.4 kJ/mol RT)   for untreated newsprint

When the temperature is taken as the time average temperature between 250°C and the final pyrolysis temperature, the Arrhenius forms for k_0 are

$k_0 = 2.5 \times 10^6$ (min^{-1}) exp(-74.7 kJ/mol $/RT$)   for acid-washed newsprint

$k_0 = 8.9 \times 10^8$ (min^{-1}) exp(-104.0 kJ/mol $/RT$)   for untreated newsprint

For acid-washed newsprint the linear correlation coefficients for both choices
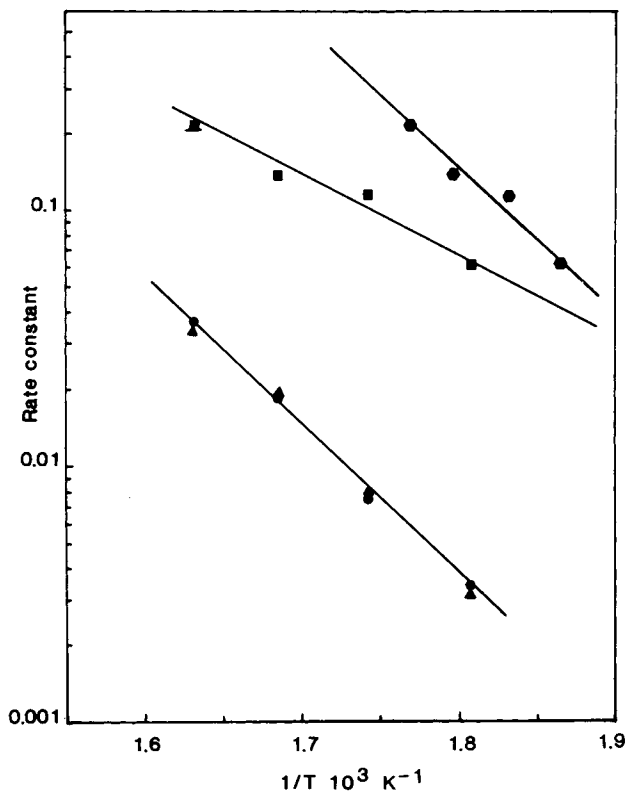
Fig. 9. Arrhenius plots for the decomposition rate constants of untreated newsprint at 280–340°C. All symbols are identical to those in Figure 8.

of temperature are 0.99. For untreated newsprint correlation coefficients are slightly higher using the final pyrolysis temperature, 0.98 vs. 0.97. Phenomenologically, either choice of temperature provides a good model for the thermal dependence of the initial reaction.

Arrhenius plots for both the zero-order, initial reaction rate constants and the isothermal, first-order rate constant for acid-washed newsprint are shown in Figure 8. Similar plots for untreated newsprint are shown in Figure 9.

DISCUSSION

We have investigated the low pressure pyrolysis of newsprint over the temperature range 260–340°C using high heating rates. A rapid initial decomposition of the newsprint has been observed. This is followed by a slower isothermal degradation that can be modeled as first order in unreacted newsprint.

Rapid initial reaction has been seen previously in pyrolysis of cellulosics. Its rate has sometimes been taken as zero order[22–24] and sometimes as first order but with an activation energy different from that at longer times.[14,21] Rates of initial decomposition have been observed to increase markedly with addition of inorganic impurities.[21,24,25] Newsprint consists of ground softwood reinforced

with some chemical pulp fibers. As such, almost 20% of the newsprint will be hemicellulose. Hemicellulose is known to be less thermally stable than the other components of ground wood—lignin and cellulose.[6] We believe the rapid initial decomposition of the newsprint is due to both degradation of lower molecular weight, less stable compounds, and reaction catalyzed by inorganic impurities.

Rogers and Ohlemiller[16] studied degradation of milled newsprint in nitrogen and air using dynamic TGA with 1°C/min and 5°C/min heating rates. They observed two distinct regions of weight loss vs. time, i.e., two separate types of reaction, with the lower temperature reaction giving more rapid weight loss. They proposed the following rate model and tested it at high (∼100°C/min) heating rates.

$$\frac{d(1 - R/W_s)}{d\theta} = (1 - R/W_s)^{-1} \frac{A}{2} \exp\left(\frac{-E_a}{RT}\right) \tag{10}$$

where $A = 1.1 \times 10^{13}$ min^{-1} and $E_a = 163$ kJ/mol. This model is not compatible with our isothermal decomposition data. Log–log plots of $(1 - R/W_s)$ vs. time are approximately linear, but their slope varies randomly between 0.1 and 0.5. Equation (10) predicts a slope of 0.5.

We can apply the above rate model to our data on initial, nonisothermal decomposition. Experimental 2-min time values of $1 - R/W_s$ for untreated newsprint are in fair accord with eq. (10) numerically integrated over the temperature vs. time curves of Figure 2. When Arrhenius values of

$$A = 7.8 \times 10^5 \text{ min}^{-1} \quad \text{and} \quad E_a = 80.4 \text{ kJ/mol}$$

are employed in eq. (10), agreement is substantially improved.

Our preferred rate parameters for eq. (10) are substantially different from those reported by Rogers and Ohlemiller. But our experimental conditions also differed considerably from theirs. We examined shredded rather than milled newsprint and worked at pressures below 1 torr rather than atmospheric pressure.

Our results can also be compared with those of similar experiments that have recently been reported involving batch pyrolyses of pure cellulose and of sawdust. Bradbury et al.[14] pyrolyzed 250-mg samples of Whatman cellulose powder at low pressure (1.5 torr) over the temperature range 259–351°C. Thurner and Mann[15] pyrolyzed 600-mg samples of oak sawdust at atmospheric pressure in flowing nitrogen over the temperature range 325–385°C. In both sets of experiments, tar and residue were separately monitored as a function of pyrolysis time and the results were interpreted in terms of first order competing rate models.

In the experiments of Bradbury et al., heat-up times were less than 2 min and little decomposition was noticed in that time period. An interesting observation was an early period of accelerating rate of weight loss. This was explained in terms of an initial reaction leading to "active" cellulose which then underwent decomposition. Activation energies for the rates of tar and char formation were 198 kJ/mol and 153 kJ/mol, respectively.

In the experiments with oak sawdust, heat-up times were of about 7 min duration. Sample weight losses of over 40% were experienced during this time. The activation energy for the overall degradation reaction was 106.5 kJ/mol. So

both in regard to early decomposition behavior and activation energy, our results for newsprint pyrolysis more closely parallel those for sawdust than for pure cellulose. This is true despite the difference in pressure between the present work (1 torr) and the experiments of Thurner and Mann (1 atm).

A 1% hydrochloric acid wash pretreatment increases the tar yield, increases the initial rate of decomposition, and slightly increases the activation energy for isothermal reaction. As shown in Table I, the dilute acid pretreatment generates a consistent 40% increase in the fractional tar yield over the temperature range 280–340°C. The char yield is scarcely altered by the acid pretreatment, indicating the enhanced tar yields arise at the expense of gaseous products.

Acid washing may influence the reaction in three ways: by removing inorganic impurities from the newsprint; by altering morphology, such as producing a more porous fibrous mat; and by chemically changing the substrate. The first two actions could cause greater tar production by minimizing catalytic degradation of newsprint to gases and by reducing secondary decomposition of tars. But only the third mechanism, chemical activity, provides a simple explanation of the observed increase in the extent of initial decomposition. The nature of this chemical activity is unclear. Considering the mild conditions of the acid pretreatment, it is unlikely that cellulose could undergo appreciable hydrolysis. However, some hemicelluloses or mechanically degraded fibers could be reactive in dilute acid at room temperature. The acid wash may also enhance the effectiveness of some inorganic impurities in catalyzing depolymerization reactions.

The ability of a dilute acid wash to increase the extent of the initial decomposition reaction may be of benefit in the conversion of newsprint to refuse-derived fuel for use as a supplement to coal or, in slurried form, to heavy fuel oil. Acid washing is now sometimes practiced with processed fuels to permit size reduction at reduced power consumption.[26] Our work suggests that such acid treatment may also change the combustion characteristics of the refuse-derived fuel.

References

1. G. M. Mallen and C. S. Finney, *AIChE Symp. Ser. No. 133*, **69**, 56 (1973).

2. D. L. Wise, S. E. Sadek, R. G. Kispert, L. C. Anderson, and D. H. Walker, *Biotechnology and Bioengineering Symposium No. 5*, C. R. Wilke, Ed., Interscience, 1975, p. 285.

3. N. W. Snyder, *AIChE Symp. Ser. No. 162*, **73**, 150 (1977).

4. P. V. Roberts, J. O. Leckie and P. H. Brunner, *ACS Symposium Series No. 76*, J. L. Jones and S. B. Reddy, Eds., American Chemical Society, Washington, D.C., 1978, p. 323.

5. M. J. Antal, Jr., H. L. Friedman and F. E. Rogers, *Combust. Sci. Technol.*, **21**, 141 (1980).

6. T. Milne, *A Survey of Biomass Gasification*, Vol. II, SERI/TR-33-239, 1979.

7. P. C. Lewellen, W. A. Peters, and J. B. Howard, 16th International Symposium on Combustion, Pittsburgh, 1977, p. 1471.

8. F. Shafizadeh and P. P. S. Chin, *ACS Symposium Series No. 43*, American Chemical Society, Washington, D.C., 1977, p. 57.

9. A. F. Roberts, *Combust. Flame*, **14**, 261 (1970).

10. T. Nguyen, E. Zavarih, and E. M. Barrall II, *J. Macromol. Sci., Rev. Macromol. Chem.*, **20**(1), 1 (1981).

11. E. P. Manche and B. Carroll, *Physical Methods in Macromolecular Chemistry*, B. Carroll, Ed., Marcel Dekker, New York, 1972.

12. J. Sestak, *Talanta*, **13,** 567 (1966).

13. P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic, New York, 1965.

14. A. G. W. Bradbury, Y. Sakai, and F. Shafizadeh, *J. Appl. Polym. Sci.*, **23,** 3271 (1979).

15. F. Thurner and U. Mann, *Ind. Eng. Chem. Proc. Des. Dev.*, **20,** 482 (1981).

16. F. E. Rogers and T. J. Ohlemiller, *Combust. Sci. Technol.*, **24,** 129 (1980).

17. F. J. Kilzer and A. Broido, *Pyrodynamics*, Gordon and Breach, New York, 1965, Vol. 2, pp. 151–163.

18. P. K. Chatterjee and C. M. Conrad, *Text. Res. J.*, **36**(6), 487–494 (1966).

19. F. Shafizadeh, T. G. Cochran, and Y. Sakai, *AIChE Symp. Ser. No. 184*, **75,** 24 (1979).

20. F. Shafizadeh, R. H. Furneaux, T. G. Cochran, J. P. Scholl, and Y. Sakai, *J. Appl. Polym. Sci.*, **23,** 3525 (1979).

21. S. L. Madorsky, V. E. Hart, and S. Straus, *J. Res. Nat. Bur. Stand.*, **56,** 343 (1956).

22. P. K. Chatterjee, *J. Appl. Polym. Sci.*, **12,** 1859 (1968).

23. A. E. Lipska and W. J. Parker, *J. Appl. Polym. Sci.*, **13,** 851 (1966).

24. W. K. Tang and W. K. Neill, *J. Polym. Sci., C*, **6,** 65 (1964).

25. S. L. Madorsky, V. E. Hart, and S. Straus, *J. Res. Nat. Bur. Stand.*, **60,** 343 (1958).

26. J. G. Abert and H. Alter, *Process in Biomass Conversion*, K. V. Sarkanen and D. A. Tillman, Eds., Academic, New York, 1979, Vol. I, p. 166.