VAPOR COMPOSITION PROFILES ESTIMATED FOR THERMALLY DEGRADING POLYETHYLENE

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ABSTRACT

Calculated vapor pressures have been used to estimate the composition of the vapor over an equimolar mixture of linear alkanes and to make inferences about the effects of pressure on the thermal degradation of polyethylene as studied using thermogravimetry. The troublesome bubbling in molten PE degrading under vacuum conditions has been related to the boiling out of molecules in the range C_{30} to $>C_{80}$. The effect of pressure in lowering the apparent overall activation energy has been ascribed to contributions from the latent heats of vaporization of molecules in the range C_{15} to $\sim C_{30}$.

INTRODUCTION

Recent determinations of the apparent overall activation energy for thermally degrading polyethylene [1] and isotactic polypropylene [2] in vacuum and under nitrogen have shown that the applied external pressure has a significant effect. Some general considerations of the effect of pressure on the results of thermogravimetric studies of polymer degradations were given in ref. 3. This paper is a semi-quantitative approach to applying those considerations to the study of thermally degrading linear polyethylene.

Table 1 gives the activation energies found [1] for thermally degrading polyethylene, together with the associated pressures, temperatures, and apparent order of reaction (calculated over small changes in extent of reaction, ~ 5%, at extents of reaction greater than 40%). The activation energies were determined using the factor-jump method of thermogravimetry [4–7], which avoids the need to specify a form for the dependence of the rate of weight loss on the extent of reaction and also determines the activation energy without any correlation with the pre-exponential factor of the Arrhenius equation. Such activation energies are expected to be relatively unbiased.

The apparent overall activation energy decreases with increasing pressure. The apparent order of reaction also decreases as the pressure increases (Table 1). This suggests that simple evaporation [8] is a significant factor. Evaporation of liquid alkanes such as $C_{36}H_{74}$ is easily shown experimentally

TABLE I

Effect of pressure on kinetic parameters of thermally degrading polyethylene

	Pressure (mm Hg of N_2 + volatiles)		
	~0.005	8	800
E (kcal mole^{-1})	65.4 ± 0.5	64.8 ± 0.3	62.6 ± 0.5
Temperature [a] (°C)	425	445	460
Bubbles?	Yes	No	No
Order of reaction	1.5 ± 0.5	0.8 ± 0.3	0.7 ± 0.3

[a] For roughly equal rates of weight loss from approximately the same size of sample at roughly the same extent of degradation at the specified pressure.

to be of zero order, depending only on the available surface area when the vapor pressure of the pure liquid is below the external pressure. When the equilibrium vapor pressure of the liquid is less than the external pressure, increasing the heat flux increases both the vapor pressure and the temperature of the liquid. However, the rate of evaporation is proportional to the rate of removal or escape of the vapor. When the vapor pressure is equal to the external pressure, normal boiling occurs in that the temperature of the liquid depends on the applied pressure and ideally cannot be increased by increasing the heating rate. Such increases provide more vapor, and when the quiescent surface area is not sufficient to allow the required amount of vapor to form, more surface area is provided through the creation of bubbles. The consequences of this were discussed in ref. 3. In practice, there is difficulty in nucleating the bubbles required in boiling because the pressure in very small bubbles is very large. This leads to superheating for boiling pure liquids. Bubble formation is greatly eased by the presence of a dissolved gas or by passing a permanent gas through the boiling liquid.

RATIONALE OF METHOD OF CALCULATION

Polyethylene degrades thermally by random scission to produce a mixture of alkanes and alkenes [9–12]. For simplicity, we will consider the vapor to be entirely alkanes since including the alkenes will not change the overall picture significantly. The method is to calculate the vapor pressures of the pure hydrocarbons, to estimate their partial pressures by assuming mole fraction values in the liquid, and then to calculate the equilibrium composition of the vapor phase above a mixture of these hydrocarbons at the specified pressure. Equimolar fractions have been used for the liquid phase. More realistic mole fractions could in principle be estimated from rate

equations for the degradation of polyethylene [13–15]. However, such calculations are beyond the scope of this paper, where the intention is to show trends.

Vapor pressures in mm Hg at the temperatures of interest may be calculated from the Antoine coefficients [16] A, B, and C as $p = 10^{[A-B/(C+T)]}$. For an ideal mixture, the vapor pressure of the ith component is equal to $m_i p_i$, where m_i is the mole fraction of compound i in the liquid and p_i is the vapor pressure of the pure substance. If $m_i p_i$ is greater than the imposed pressure, then the ith component will be unstable with respect to boiling out of the liquid and, other things being equal, will boil out of the liquid with a rate related to the difference between the imposed and vapor pressures and to its rate of diffusion through the liquid. Here, however, we assume that the delay between formation of such a component in the degradation of polyethylene and its leaving the liquid phase is negligibly small. Under these circumstances, its contribution, l_i, to the weight loss will be proportional to n_i, the number of its carbon atoms.

If $m_i p_i$ is less than the imposed pressure, then compound i will evaporate "normally", i.e., it will be below its boiling point. The rate of its evaporation will be dependent directly on the rates of diffusion and removal of volatiles and inversely on the imposed pressure. If an appreciable rate of removal of volatiles is assumed, and all species are assumed to have the same rate of diffusion, then the rate of evaporation for the ith component may be considered to be proportional to $m_i p_i$. The contributions to the weight loss from the evaporating compounds can be put on the same scale as those from the boiling compounds by representing the contribution of the ith component to the weight loss as $l_i = n_i m_i p_i / p$, where p, the imposed pressure, is used as a normalizing factor. For boiling compounds $m_i p_i / p$ was effectively given the relative value 1. This will be the case for all $m_i p_i \geqslant p$. Since polyethylene degrades by random scission, all molecular fragments may be assumed to be produced in equal quantities. Hence, the total weight loss will be Σl_i, summed over all values of i, and the contribution of compound i will be $100 \, l_i / \Sigma l_i \%$. The relative amount, f_i, of molecular fragments i in the vapor will be given by $f_i = 1$ or $m_i p_i / p$, whichever is smaller. From a summation over all molecular lengths considered, vapor phase mole fractions, v_i, can be estimated from $v_i = f_i / \underset{i}{\Sigma} f_i$. The average number of carbon atoms per molecule in the vapor phase is given by $\underset{i}{\Sigma} v_i n_i$.

A simple BASIC program to perform the appropriate calculations was written and is given in Appendix 1. The components considered range from $C_4 H_{10}$ to $C_{100} H_{202}$. The lower limit was imposed because smaller species are minor components of the weight loss process following degradation of polyethylene. The upper limit is the limit of the tables in ref. 16. Since the program is intended to compare two thermogravimetric runs, it calculates vapor pressures for two specified temperatures and then estimates the

contributions to the weight loss at the specified pressures. For convenience, only the even alkanes are considered. For this reason, the calculated contribution to the weight loss is divided by two in the program, because half the weight loss would be due to the odd alkanes.

RESULTS

Figure 1 shows the contribution to the weight loss under the conditions of 425°C, 0.005 mm Hg (1 mm Hg = 133 pascals); 445°C, 8 mm Hg; and 460°C, 800 mm Hg (the conditions in Table 1) for an ideal equimolar mixture of the hydrocarbons C_4 to C_{100}. The difference in profiles is striking. Almost no hydrocarbons boil at 460°C, 800 mm Hg, whereas in the near-vacuum case, boiling is observed up to $\sim C_{85}$.

In vacuum conditions, unsteadiness in the sample weight is observed and has been attributed [1,3] to bursting bubbles. No shocks to the balance are observed at overall pressures of 8 and 800 mm Hg of N_2. A reasonable explanation is as follows. We note from Fig. 1 that normal boiling ceases at $\sim C_{29}$ for 8 mm Hg and 445°C, at $\sim C_8$ for 800 mm Hg and 460°C, and at $\sim C_{85}$ for 0.005 mm Hg and 425°C for the hypothetical mixture of hydrocarbons. Thus the vacuum case requires that molecules up to C_{85} be forced rapidly out of the liquid. The slowness of diffusion for the largest of these molecules (C_{30} to C_{85} were not under boiling conditions at 8 mm Hg and 445°C) to the quiescent surface must require the formation of "local surface"
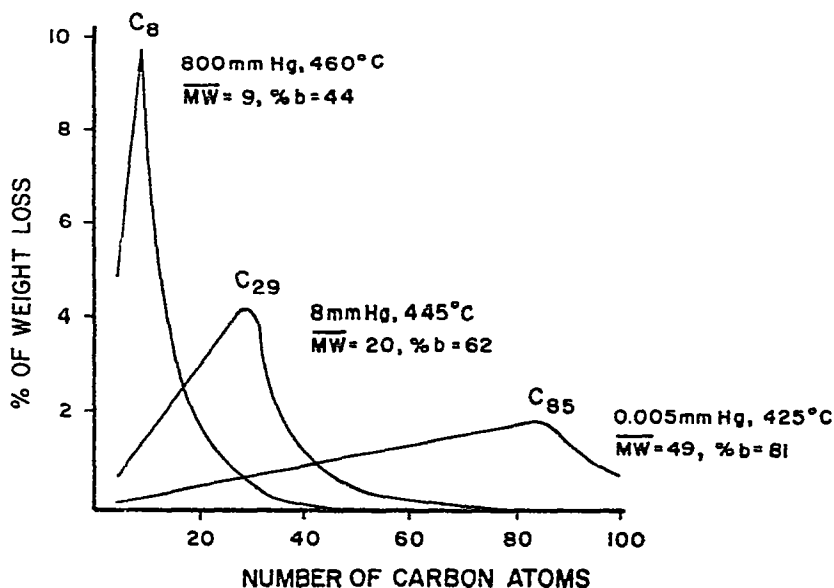

Fig. 1. The implied contribution to the weight loss from an equimolar mixture of linear alkanes for conditions as indicated. The largest alkane unstable with respect to boiling is noted in each case. $\overline{MW}$ = average number of carbons in the vaporized molecules, %b = the percentage of the weight loss which is ascribed to molecules unstable with respect to boiling.

in the form of bubbles, so that they may be volatilized. Because most nucleation is heterogeneous, these bubbles would form on the wall of the sample cup.

The smaller molecules will have very large vapor pressures at the temperatures of interest and are so unstable with respect to boiling that they are able to enter even very small bubbles. Thus the small molecules will act as a dissolved permanent gas. In this sense, the smaller molecules "nucleate" the bubbles, which then accept the larger molecules as the bubble size increases. The number of bubbles is related to the amount of small molecules, acting as permanent gases. For very small bubbles with high internal pressures, the number of such molecules is independent of the pressure, but is a function of the temperature. The temperatures required for a given rate of weight loss are lower in vacuum than under higher imposed pressures, and therefore fewer small molecules will be produced under vacuum conditions than under higher pressures. Therefore, to a first approximation, fewer bubbles will be nucleated in vacuum. However, more species are volatile in vacuum than under the higher pressures, and the bubbles will grow very rapidly in vacuum because (i) many of the potentially volatile molecules can evaporate only into large bubbles or from similar surfaces, and (ii) the opposing pressure is very low. Also, the elasticity and viscosity of the molten polymer will allow these bubbles to grow to a significant size, and when they burst they will impart shocks to the thermogravimetric balance because of the momentary imbalance of forces on opposite sides of the bursting bubble and because of the "snapping back" of the liquid surface of the bubble. Viscosity and elasticity are higher, the higher the average molecular weight of the liquid, and thus will be higher for the vacuum case.

The effect of pressure on the overall apparent activation energy of the weight loss process in degrading polyethylene can be rationalized as follows. The compounds in the "tail" (Fig. 1), which represents normal evaporation rather than boiling, will be formed at the same rate as the boiling compounds in the degradation of polyethylene, but will not completely evaporate. Presumably their concentration will build up and they will be removed by later evaporation and by further degradative attack. As they evaporate, their contributions to the overall activation energy will be their latent heats of vaporization. This is between 10 and 50 kcal mole^{-1}, depending on the molecular length and the temperature. Since the activation energy for the chain breaking process in polyethylene is thought to be in excess of 65 kcal mole^{-1} [1], contributions from latent heats of vaporization will lower the apparent overall activation energy. The latent heats of vaporization for the boiling molecules will not be important because there the rate determining step will be their production in the degradation process rather than their evaporation.

For the vacuum case, most of the weight loss is achieved by normal boiling. For an equimolar mixture of species in the range C_4 to C_{100}, the

simplified scheme used here estimates that 81% of the weight loss is by boiling at 425°C and 0.005 mm Hg pressure. The contribution from the latent heats of vaporization of the large molecules in the tail will be small and the latent heats themselves will be fairly near the 65 kcal mole^{-1} (1 kcal mole^{-1} = 4.18 kJ mole^{-1}) observed for weight loss in vacuum. The overall activation energy should then be quite close to the activation energy for the degradative process of polyethylene itself. For the imposed external pressure cases, there is some weight loss from the evaporation of small and medium sized molecules, which will have much lower latent heats of vaporization (in the range of 10–30 kcal mole^{-1}) and thus there will be some lowering of the overall activation energy. Only 44% of weight loss is estimated to occur under boiling conditions for 460°C and 800 mm Hg pressure, and 62% at 445°C and 8 mm Hg pressure. According to these estimates, a significant part of the weight loss should occur by evaporation, and an appreciable lowering of the overall activation energy would be expected in Table 1. However, the actual lowering is fairly small for polyethylene (but appears to be larger for polypropylene [2]). There are several complicating factors. One is that non-boiling but potentially evaporating molecules are removed by degradation as well as by evaporation. Another is that diffusion rates will effectively cause the whole weight loss profile to be multiplied by some function of the inverse of the molecular weight for each component and will reduce the effective lengths of the evaporative tails in Figs. 1–4 and thus will reduce the percentage of weight loss due to evaporation. There is also the question of assigning appropriate mole fractions for the volatiles in degrading polyethylene. Because of this question, no attempt was made to model accumulation of the "tail" compounds during the degradation.

If the observed [1] activation energy of 65.4(5) kcal mole^{-1} is assumed to apply to the process of producing small molecules from long polyethylene molecules, then the temperatures in Table 1 and Fig. 1 correspond to degradation rates of ~ 1:4:10. These temperatures are for approximately equivalent rates of weight loss under the pressures specified in Table 1. Since the weight loss is independent of whether methylene units are joined or not this means that, for equal overall rates of weight loss, samples which are degrading faster because of their higher temperature must be volatilizing shorter molecules. In particular, the average molecular weights in the vapor phase are 1:1/4:1/10 = 1:0.25:0.1 at these temperatures.

The calculated average number of carbon atoms per volatilizing molecule is given in Fig. 1 as 49:20:9 for the three cases considered. These values lie in the ratio 1:0.41:0.18. The last two are in approximately the correct ratio to each other. The first, for the near vacuum case, is somewhat too low, as expected because the tail obviously should include molecules longer than C_{100}, but these molecules were not included in the calculations because their Antoine coefficients are not given in the tables. Also, the total pressure was probably not exactly 0.005 mm in the vacuum case and the upper limit of
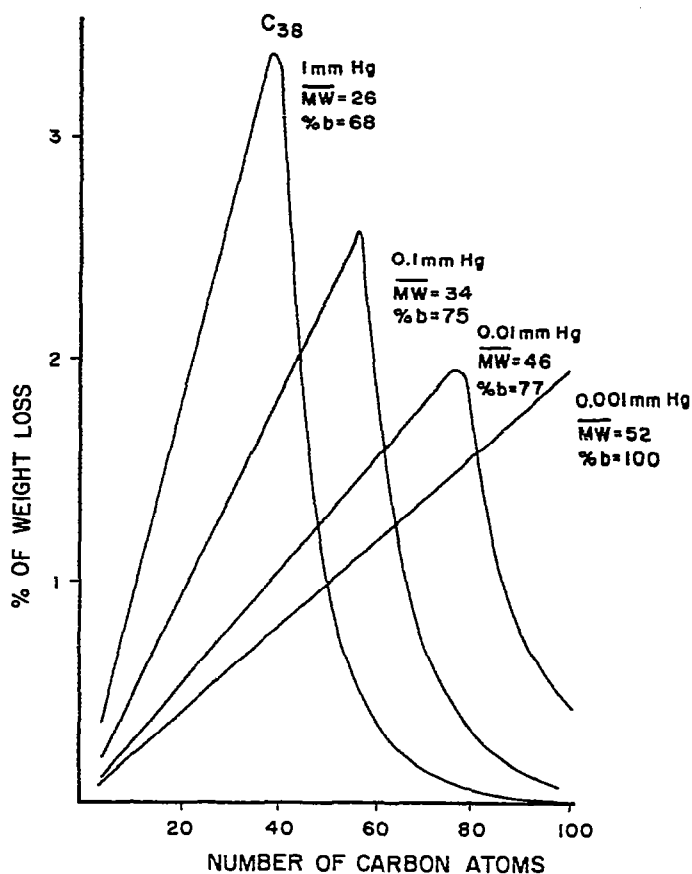
Fig. 2. Vapor composition profile and implied contribution to the weight loss from an equimolar mixture of linear alkanes under several imposed total pressures at 425°C. Notation as in Fig. 1.

boiling molecules is very sensitive to the total pressure in this region. A lower pressure would give a higher average molecular weight and a greater range of boiling molecules. Figures 1 and 2 predict considerable volatility under vacuum conditions above $\sim 400°C$ for molecules up to C_{100}, the longest molecule considered here. In practice $C_{94}H_{190}$ has been observed [17] to evaporate without decomposition at rates comparable to those used in thermogravimetry. Figure 2 gives the calculated profiles of volatiles for imposed pressures of 0.001, 0.01, 0.1, and 1 mm Hg, all at 425°C. Even for this series of pressures, each of which is nominally small when compared with 800 mm Hg for example, there are important differences in the volatile profiles.

If the important aspect is to minimize the tail representing "normal evaporation" as opposed to "normal boiling", then Fig. 2 shows that the appropriate conditions are that the pressure should be as low as possible. Figure 3 shows that the temperature has less effect in reducing the proportion of weight loss by evaporation but has a large effect on the size of

molecules volatilized and hence on the propensity for explosive bubble formation. The results also indicate the extent to which the assumption of a sharp cut-off in the size of molecules volatilized is realistic. The largest molecule evaporating in degradation in vacuum was assumed to have $L \sim 70$ carbon atoms in the Wall–Simha treatment [13,18]. Suehiro and O'Shima [14] estimated an upper limit of $L \sim 26$ carbon atoms for evaporation in an inert atmosphere at 420°C. We see clearly that this upper limit is indeed dependent on the imposed pressure and is actually a distribution. Also, as Wall et al. [13] remarked, it may be expected to vary with extent of degradation. The pressure and degradation dependence probably explain much of the discrepancy in degradation products reported in refs. 9–12. It is obvious from the figures that the cut-off is sharpest at very low pressures, and that it changes markedly with temperature.

Figure 3 also indicates clearly the change in vapor composition solely on increasing the temperature. This purely physical effect will usually be greatest in dynamic heating rate experiments, where the temperature range is
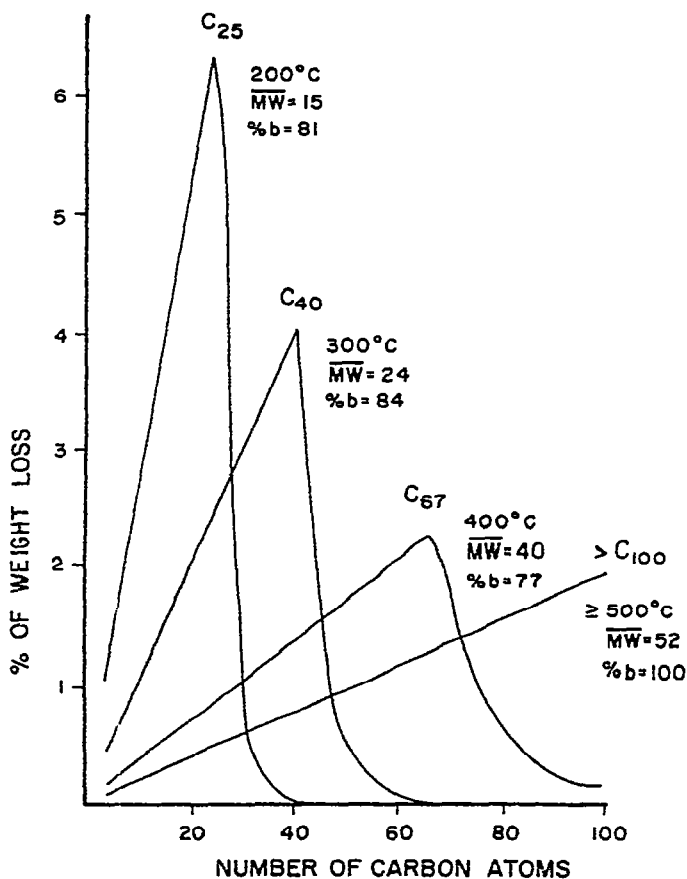

Fig. 3. Vapor composition profile and implied contribution to the weight loss from an equimolar mixture of linear alkanes at various temperatures and under a total pressure of 0.01 mm Hg. Notation as in Fig. 1.
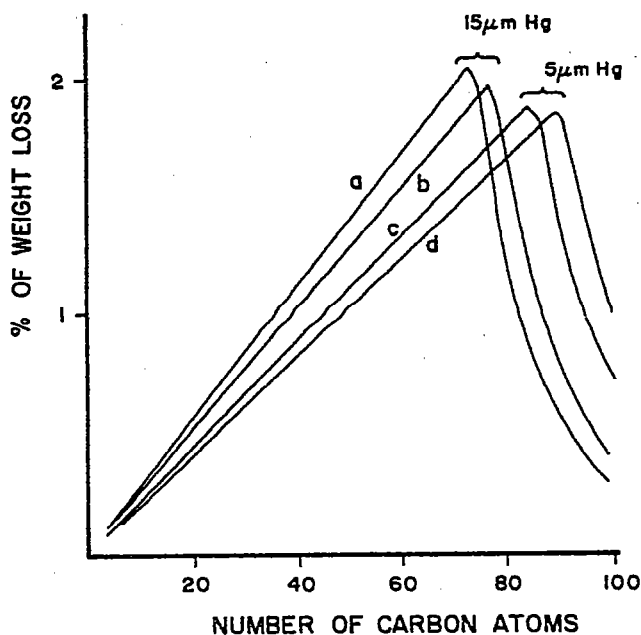
Fig. 4. Vapor profile and implied weight loss contributions for an equimolar mixture of linear alkanes under factor-jump thermogravimetry type conditions, and at two imposed pressures: (a) 425°C, 15 μm, $\overline{MW}$=44, %b=76, C_{74}; (b) 433°C, 15 μm, $\overline{MW}$=45, %b=77, C_{77}; (c) 425°C, 5 μm, $\overline{MW}$=49, %b=82, C_{85}; (d) 433°C, 5 μm, $\overline{MW}$=50, %b=83, C_{90}. Notation as in Fig. 1.

usually larger than in isothermal experiments. The case for the type of multiple-isothermal experiment used in factor-jump thermogravimetry is shown in Fig. 4. The sample is subjected to successive isothermal treatments, separated by +8°C, −5°C, +8°C, and so on. Typical temperatures for our studies of thermally degrading polyethylene were 425°C and 433°C. The pressure was typically 5 μm (0.005 mm). The difference in vapor composition is noticeable, but is small. Average numbers of carbon atoms per vaporized molecule are in the region of C_{50}, with boiling up to $\sim C_{90}$ (see Fig. 4).

CONCLUSIONS

Calculated vapor pressures have been used in a first-approximation model of the vapor above thermally degrading polyethylene. The "normal boiling" of large molecules in the range C_{30} to $> C_{90}$ probably forces the rapid growth of bubbles in polyethylene degrading at low pressures, and the bubbles will grow to significant size because the liquid is relatively elastic.

The trend of decreasing apparent overall activation energy with increasing pressure is ascribed to contributions of low latent heats of vaporization from molecules up to $\sim C_{30}$ depending on the imposed pressure. The trends of vapor composition for various temperatures and pressures are given. In general, both the temperature and the pressure should be as low as possible to minimize the contribution of the latent heats of vaporization to the overall activation energy and interference from bubbles in the molten degrading polymer.

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APPENDIX I

A BASIC program to calculate the vapor pressures and vapor composition over mixtures of hydrocarbons

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10 REM PROGRAM TO GET VOLATILE PROFILE FOR RANDOM SCISSION
20 REM  JUNE 1981
30 DIM H(100),A(100),B(100),C(100),V1(100),V2(100),L1(100),L2(100)
40 DIM M1(100),M2(100)
50 DIM A$(1)
60 PRINT " INPUT TEMPERATURES AND PRESSURES OF DEGRADATIONS"
70 PRINT " TEMPERATURES IN DEGREES CELCIUS, PRESSURES IN MM HG"
80 PRINT " TEMPERATURE FOR FIRST DEGRADATION?"
90 INPUT T1
100 PRINT " PRESSURE OF FIRST DEGRADATION IN MM HG?"
110 INPUT P1
120 PRINT " TEMPERATURE FOR SECOND DEGRADATION?"
130 INPUT T2
140 PRINT " PRESSURE OF SECOND DEGRADATION IN MM HG?"
150 INPUT P2
160 PRINT "GIVE HIGHEST MOLECULAR SPECIES? FROM C4 UP TO C?"
170 INPUT N
180 M=INT((N-4)/2+1.1)
190 PRINT " FIRST DEGRADATION AT T=";T1;", P=";P1
200 PRINT " SECOND DEGRADATION AT T=";T2;", P=";P2
210 PRINT " SPECIES GO FROM C4 TO C";N
220 PRINT " IS THIS OK? Y OR N?"
230 INPUT A$
240 IF A$<>"Y" GOTO 60
250 PRINT ON (7)" FIRST DEGRADATION AT T=";T1;", P=";P1
260 PRINT ON (7)" SECOND DEGRADATION AT T=";T2;", P=";P2
270 PRINT ON (7)"SPECIES GO FROM C4 TO C";N
280 PRINT "CARBONS","VAP PRESS","WT LOSS","VAP PRESS","WT LOSS"
290 S1=0
300 S2=0
310 B1=0
320 N1=0
330 B2=0
340 N2=0
350 FOR I=1 TO M
360 READ H(I),A(I),B(I),C(I)
370 V1(I)=10^(A(I)-B(I)/(C(I)+T1))
380 V2(I)=10^(A(I)-B(I)/(C(I)+T2))
390 V1(I)=V1(I)/(2*M)
400 V2(I)=V2(I)/(2*M)
410 IF V1(I)>=P1 THEN L1(I)=H(I)
420 IF V1(I)>=P1 THEN B1=B1+L1(I)
430 IF V1(I)>=P1 THEN M1(I)=1
440 IF V1(I)<P1 THEN L1(I)=V1(I)*H(I)/P1
450 IF V1(I)<P1 THEN N1=N1+L1(I)
460 IF V1(I)<P1 THEN M1(I)=V1(I)/P1
470 IF V2(I)>=P2 THEN L2(I)=H(I)
480 IF V2(I)>=P2 THEN B2=B2+L2(I)
490 IF V2(I)<P2 THEN L2(I)=V2(I)*H(I)/P2
500 IF V2(I)>=P2 THEN M2(I)=1
510 IF V2(I)<P2 THEN N2=N2+L2(I)
520 IF V2(I)<P2 THEN M2(I)=V2(I)/P2
530 S1=S1+L1(I)
540 S2=S2+L2(I)
550 NEXT I
560 A1=0
570 A2=0
580 M3=0
590 M4=0
600 FOR I=1 TO M
610 L1(I)=L1(I)/(S1*2)
620 L2(I)=L2(I)/(S2*2)
630 PRINT H(I),V1(I),L1(I),V2(I),L2(I)
640 A1=A1+M1(I)*H(I)
650 A2=A2+M2(I)*H(I)
660 M3=M3+M1(I)
```

```
670 M4=M4+M2(I)
680 NEXT I
690 B1=100*B1/(B1+N1)
700 N1=100-B1
710 B2=100*B2/(B2+N2)
720 N2=100-B2
730 PRINT B1;"% OF WT LOSS BY BOILING,":N1:"% BY EVAPORATION, CASE 1"
740 PRINT B2;"% OF WT LOSS BY BOILING,":N2:"% BY EVAPORATION, CASE 2"
750 PRINT ON (7)B1;"% WT LOSS BY BOILING":N1;"% BY EVAPORATION CASE 1"
760 PRINT ON (7)B2;"% WT LOSS BY BOILING":N2;"% BY EVAPORATION CASE 2"
770 A1=A1/M3
780 A2=A2/M4
790 PRINT " THE AVERAGE MWS OF THE VOLATILES ARE":A1:" AND":A2
800 PRINT ON (7)" THE AVERAGE MWS OF THE VOLATILES ARE":A1:" AND":A2
810 PRINT ON (7)"CARBONS","VAP PRESS","WT LOSS","VAP PRESS","WT LOSS"
820 FOR I=1 TO M
830 PRINT ON (7)H(I),V1(I),L1(I),V2(I),L2(I)
840 NEXT I
850 WFM 7
860 DATA 4,6.80776,935.77,238.789
870 DATA 6,6.87601,1171.17,224.408
880 DATA 8,6.91868,1351.99,209.155
890 DATA 10,6.94363,1495.17,193.858
900 DATA 12,6.99795,1639.27,181.835
910 DATA 14,7.013,1740.88,167.72
920 DATA 16,7.02867,1830.51,154.45
930 DATA 18,7.0022,1894.3,143.3
940 DATA 20,7.1522,2032.7,132.1
950 DATA 22,7.0842,2054,120.1
960 DATA 24,7.0976,2112,109.6
970 DATA 26,7.1096,2164.3,99.6
980 DATA 28,7.1205,2211.6,90
990 DATA 30,7.1304,2254.6,80.9
1000 DATA 32,7.14,2296.4,71.6
1010 DATA 34,7.1482,2334.9,63.4
1020 DATA 36,7.1558,2364.6,55.1
1030 DATA 38,7.1627,2394.7,47.4
1040 DATA 40,7.1691,2422.3,40.1
1050 DATA 42,7.175,2447.7,33
1060 DATA 44,7.1804,2471.2,26.3
1070 DATA 46,7.1854,2493,19.8
1080 DATA 48,7.19,2513.1,13.7
1090 DATA 50,7.1944,2531.8,7.8
1100 DATA 52,7.1984,2549.2,2.1
1110 DATA 54,7.2021,2565.5,-3.3
1120 DATA 56,7.2056,2580.6,-8.5
1130 DATA 58,7.2089,2594.7,-13.5
1140 DATA 60,7.2119,2607.9,-18.3
1150 DATA 62,7.2148,2620.2,-22.9
1160 DATA 64,7.2174,2631.8,-27.3
1170 DATA 66,7.2199,2642.7,-31.6
1180 DATA 68,7.2223,2652.9,-35.6
1190 DATA 70,7.2245,2662.5,-39.5
1200 DATA 72,7.2266,2671.6,-43.3
1210 DATA 74,7.2286,2680.1,-46.9
1220 DATA 76,7.2304,2688.2,-50.4
1230 DATA 78,7.2322,2695.8,-53.7
1240 DATA 80,7.2338,2702.9,-56.9
1250 DATA 82,7.2354,2709.7,-60
1260 DATA 84,7.2369,2716.2,-63
1270 DATA 86,7.2383,2722.2,-65.8
1280 DATA 88,7.2396,2728,-68.6
1290 DATA 90,7.2408,2733.5,-71.3
1300 DATA 92,7.242,2738.7,-73.8
1310 DATA 94,7.2432,2743.6,-76.3
1320 DATA 96,7.2443,2748.3,-78.7
1330 DATA 98,7.2453,2752.8,-80.9
1340 DATA 100,7.2463,2757.1,-83.1
1350 STOP
1360 END
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Lines 10–280 are for establishing the temperatures and pressures while giving the user the possibility of changing his mind or correcting mistakes. Lines 290–340 set some counters to zero. The vapor pressures are calculated on lines 370 and 380 and are corrected for mole fraction on lines 390 and 400. In lines 410–520, L1 and L2 are the contributions to the weight loss for conditions 1 and 2, B1 and B2 boiling contributions to the weight loss, N1 and N2 are the non-boiling (evaporative) contributions to the weight loss, and M1 and M2 are the relative mole fractions in the vapor. Each species i has its own values of these quantities.

Lines 530 and 540 sum up the total weight loss. Lines 610 and 620 calculate the fraction of weight loss due to each species, and lines 640–670 calculate quantities related to the number of carbon atoms in the vapor (A1 and A2) and the number of molecules (M3 and M4). Lines 690–720 calculate the percentages of weight loss due to boiling and non-boiling, lines 770 and 780 calculate the average number of carbon atoms per molecule in the vapor phase, and the other lines print the information on the terminal and on a disc file 7 (so that plots or a printed record can later be made). Lines 860–1340 contain the number of carbon atoms and the three Antoine coefficients for the even-numbered alkanes C_4H_{10} to $C_{100}H_{202}$.

The aim has been to make the program easily understood rather than efficient.