

Thermodynamic and Kinetic Variables in Tobacco Pyrolysis and their influence on the Relationship between Smoking and Health.

J. A. E. Bell, PhD⁽¹⁾ D. H. Laing⁽²⁾

ABSTRACT

Statistical analysis of recent data on the mortality rates of pipe, cigar and cigarette smokers showed that the mortality ratio of smokers could be best described in terms of the dose rate (volume of smoke per day), length of exposure and toxicity of the smoke. When the toxicity of cigarette smoke was defined as one, the toxicity of pipe smoke was found to be $0.07 \pm .11$ and of cigar smoke $0.28 \pm .13$. No reasonable explanation of this difference in toxicity has been proposed. A hypothesis that the toxicity of the smoke is controlled by the combustion conditions during pyrolysis of the tobacco is advanced.

The mode of the combustion of cigarettes, pipes and cigars and some of the chemical properties of their smoke were studied. Substantial differences between the composition of their respective gaseous constituents and that of their particulate phase is demonstrated. The optical tar density produced by tobacco pyrolysis is proportional to the square of the rate of heating of the tobacco multiplied by the mass of tobacco burned per puff. There appears to be a quantitative link between the optical tar density and the toxicity of the smoke to mortality. It is also demonstrated that

100086657

by altering the combustion characteristics of a cigarette that the properties of the smoke are changed so that the expected mortality ratio of male cigarette smokers aged 45 to 65 will be reduced from 2.1 to less than 1.1 for an average daily dose of 28 cigarettes at 25 cc/puff with an average age of starting to smoke of 19 years.

- (1) Senior Research Eng., The International Nickel Company
of Canada, Limited, Sheridan Park, Clarkson, Ont.
- (2) Technologist, University of Toronto, Dept. of Met. & Mat. Sc.

Introduction

A statistical analysis of recent observations (1), (2), (3) and (4) on the influence of pipe, cigar and cigarette smoking on health is undertaken in the appendix. This analysis showed that the toxicity of pipe smoke was 15 times lower than the toxicity of cigarette smoke, and that cigar smoke was 3 times less toxic at the same smoke dose rate and length of exposure.

No really satisfactory explanation of this difference in toxicity has been advanced and it is hypothesized in the appendix that the toxicity of the smoke is controlled by the combustion conditions of the pyrolysis of the tobacco. This portion of the paper describes an experimental investigation of the influence of the pyrolysis conditions of the tobacco on the properties of the smoke.

100086658

Description of Tests

The combustion of tobacco is a complex process involving both destructive distillation and oxidation reactions. Two major phases are present in the smoke - a gaseous phase and a liquid particulate phase. From thermodynamic considerations it is well known that the time - temperature relationships which exist during the combustion are the important variables governing the composition of both the particulate and gaseous phases.

In order to minimize the influence of tobacco type on the combustion mode, the same tobacco was employed in the pipe as in the cigarette. The measurements on cigars, of course, precluded the possibility of the use of the same tobacco. Chromel-Alumel (0.006" Diameter) thermocouples were used to continually record the time-temperature relationships in the combustion of the tobacco. Readings of the maximum temperature attained during the draw cycle are difficult to obtain, and admittedly the even temperature during the idle (no puff) cycle shown in Table 1 are low because fine enough thermocouples were not employed (5). The temperature differences are however, quite significant.

In the cigarette the maximum temperature of over 730°C in the fire ball occurs at a point approximately 0.6 cms ahead of the

100086659

burning interface of the paper. The particulate phase in the smoke is not produced near this maximum temperature zone and the particulate phase of the smoke becomes gaseous if heated over 500°C and substantially gaseous over 300°C . Thus the maximum temperature in the fire ball can not be the primary factor controlling the composition of the particulate phase.

Under uniform puffing conditions or at idle the rate of heating of the tobacco is constant from approximately 150°C to 500°C i. e. the time versus temperature trace on a recorder is a straight line.

The linearity of the time - temperature trace during puffing or idling is also shown by Touey and Mumpower (5). In the study of reaction rate kinetics and in irreversible thermodynamics it is well known that the products from any reaction are controlled by the time and temperature variables. The only parameter reflecting a time - temperature relationship in smoking which can be measured in the 150°C - 500°C range is the rate of heating of the tobacco; and this parameter should be the major thermodynamic or kinetic variable controlling the particulate phase composition. The rate of heating of the tobacco found in various ways of smoking tobacco is shown in Table 1 as a function of the number of puffs per minute at idle and also during the puff

100086660

cycle. Each reading is averaged from 10 to 30 measurements covering a wide variety of brands. The rate of heating of the tobacco in the range 150°C - 500°C will be more independent of the thermocouple size than the absolute temperature measurement and the accuracy of the couples used in these experiments should be quite sufficient.

The velocity of the burning interface is shown in Table 1 at idle and during puffing, as well as the mass of tobacco burned per puff cycle.

The number of puffs per device was measured under standard conditions - the cigarette and cigar at two puffs per minute, and the pipe at eight puffs per minute. The puff rate during pipe smoking must be measured at a puff rate over two puffs per minute or the combustion of the tobacco will terminate as indicated in Table 1.

Analysis of the gaseous phase composition was undertaken using normal gas chromatographic procedures and the results are shown in Table 1.

A detailed study of the particulate phase was not undertaken. Indeed, it is not possible to know which combination of compounds is important from a health standpoint. The major purpose of these tests was to indicate that alteration of the variables of combustion changes the properties of the particulate phase.

100086661

Total Particulate Matter (TPM) tests were carried out in a major Canadian tobacco company on conventional cigarettes and cigarettes modified by compression as described below. Both cigarettes had the same overall pressure drop and samples of 100 cigarettes were employed. The results had to be compared on a per puff basis as the compressed cigarette burned longer (see Table 1). Another indication of the hydrocarbons content of the smoke is what may be termed the optical tar density (OTD). The smoke from the smoking device was scrubbed by a given amount of a methyl hydrate (in these tests 25 cc's) and the absolute absorbance of the solution compared to pure methyl hydrate was measured on a recording spectrophotometer. The absorbance of the solution in the visible spectrum is directly proportional to the amount of coloured hydrocarbons in the smoke. Fortunately, the relative absorbance between all types of smoke studied is constant across the entire visible spectrum so that the absorbance of the solutions can be compared at any wave length in the visible spectrum. In Table 1 the relative absorbance measured at 450 millimicrons is shown on a scale with the value for smoke from the cigarette adjusted to a value of 100. The results were measured after smoking each device to approximately a normal butt length and reported on a per puff basis.

100086662

As noted in Table 1 the optical tar density in the smoke from the pipe and cigar is remarkably lower than the smoke from cigarettes. In addition it should be noted that the rate of heating in the tobacco is correspondingly lower. To further experimentally substantiate this apparent relationship, cigarettes were altered to change the rate of heating of the tobacco. Compression of the tobacco and placing of a small longitudinal hole down the cigarette in order to secure proper "drawing" characteristics appears to be the most effective method to produce the change.

Cigarettes were compressed by 1/3 in a longitudinal direction without changing the cross sectional area or wrinkling the paper, pierced longitudinally by a 3/32 inch rod, and subjected to the same tests as the usual smoking devices and the results indicated in Table 1 under "Comp. " cigarette. Cigarette tobacco was also rerolled to a density 1/3 greater than normal cigarettes, pierced longitudinally, and tested as shown in Table 1 under "Reconst. " cigarette.

Discussion

In the introduction it was postulated that the properties of the smoke from tobacco should depend on the thermodynamic and kinetic variables of the pyrolysis to which the tobacco is subjected. If this postulate is correct then there should be a quantitative

100086663

relationship between the smoke properties and these variables. The rate of heating of tobacco during the puff cycle was shown to be one of the most important thermodynamic and kinetic properties. The rate of heating of the tobacco at idle could have been selected to make a similar demonstration. From Table the most significant difference in the smoke produced was shown to be the optical tar density. Thus the relative optical tar density (ROTD) should bear a functional relationship to the rate of heating of the tobacco (HR) or:

$$\text{ROTD} = f(\text{HR})$$

The amount of coloured hydrocarbons per puff should also be expected to be linearly related to the mass of tobacco burned per puff (M/P), thus:

$$\text{ROTD} = f((\text{HR}) \times (\text{M/P}))$$

Statistical analysis of the results shown in Table indicate that the simple best fit equation is:-

$$\text{ROTD} = -0.22 + 0.225 \times ((\text{HR})^2 \times (\text{M/P})) \pm 10.8$$

This equation is shown graphically in Figure 1, along with the experimentally determined points. The probability that there is no statistical correlation between ROTD and $(\text{HR})^2 \times \text{M/P}$ is less than 1 in 100. The standard error of the best fit equation is 10.8 and the correlation coefficient between ROTD and $(\text{HR})^2 \times (\text{M/P})$

100086664

is 0.976 (a perfect correlation is 1.0). The above equation also satisfies the criteria that when the tobacco is not burning, i. e. $M/P = 0$ or $HR = 0$, then $RPTD = 0$.

The relative optical tar density per puff is only an indicative property of the particulate phase. From thermodynamic reasoning it is possible to assert that there will be similar mathematical relationships between the combustion variables i. e. the rate of heating of the tobacco, HR, and any of the compositional variables. Thus, the conclusion is of general validity that the composition of smoke produced by tobacco pyrolysis is dependent upon the thermodynamic variables of the pyrolysis and the hypothesis propounded in the introduction is substantiated.

In the appendix the best fit equation which fits all of the mortality data of all male smokers aged 45 to 65 was found to be:

$$MR = .93 + .032(TOXICITY)(DOSE RATE \times 10^{-4})^{1/3} \times (55 - AS)$$

where:-

MR = Morlatily ratio (ratio of deaths of smokers to non-smokers of the same age)

DOSE RATE = cc of smoke inhaled per day

AS = age started smoking.

100086665

The best values of the toxicity were found to be; for cigarette smoke - $1.07 \pm .07$ (defined), for pipe smoke - $0.07 \pm .11$ and for cigar smoke - $0.28 \pm .13$.

If the optical tar density issuing from the smoking device per puff significantly affects the mortality ratio of the smoker then there should be a relationship between the relative tar density and the toxicity. This comparison is indicated in Table 2.

TABLE 2

Comparison of the Relative Optical Tar Density to the Relative

Smoke Toxicity

<u>Device</u>	<u>Relative Optical Tar Density/100</u>	<u>Relative Smoke Toxicity</u>
Cigarette	1.00	$1.00 \pm .07$
Cigar	0.40 to 0.50	$0.28 \pm .13$
Pipe	0.03 to 0.08	$0.07 \pm .11$
Reconst. Cigarette	0.11	.11

Thus with a high degree of confidence it can be stated that the toxicity of the smoke is equal to the relative optical tar density.

100086666

The optical tar density is only one indication of the potential health hazard to the smoker and a more general hypothesis that the smoke toxicity is a function of the thermodynamic variables alone is more fitting. Since a relationship between the rate of heating and the burning rate with the optical tar density was shown to exist at the 99% confidence level and since the optical tar density is directly related to the smoke toxicity it is possible to state with a large degree of confidence that there is a relationship between the health hazard or toxicity of smoking and the thermodynamic and kinetic variables of the pyrolysis of tobacco. In addition, it can be asserted that the important variables controlling the composition of the particulate phase are the rate of heating of the tobacco and the rate of burning of the tobacco. It is interesting to note that if cigarettes were produced so that they exhibit similar properties to those shown in columns 4 and 5 of Table 1 then the expected mortality ratio of male cigarette smokers aged 45 to 65 with an average daily dose rate and length exposure would be lowered from 2.1 to 1.1.

Summary

As shown in the appendix cigarette smoking is a serious health hazard while pipe and cigar smoking is not. No evidence has been advanced which can explain this difference as discussed in the

100086667

appendix. The only possible reason was shown to be a variation of smoke composition produced by different burning conditions in the cigarette, pipe and cigar.

Some of the chemical properties of the cigarette, cigar and pipe smoke were studied and a large difference was found. For instance, the optical tar density of cigarette smoke was found to be 20 times higher than in pipe smoke. A direct relationship between the optical tar density and the toxicity for all types of smokers was established. Thus it can be concluded that:

the greater health hazard of cigarette smoking compared to pipe and cigar smoking derives from a different smoke composition, and that:

the optical tar density is an important index of the health hazard or smoke toxicity.

The amazing difference in optical tar density between pipe and cigarette smoke was shown to depend quantitatively on the rate of heating of the tobacco and the rate of burning during combustion.

By altering the construction of a cigarette it was possible to approach the burning conditions in the pipe. Smoke from the altered cigarettes had optical tar densities similar to that of pipe smoke. From these observations it can be concluded that:

100086668

the combustion conditions control the smoke composition, and that:

cigarettes can be altered so that the smoke and combustion conditions are substantially the same as pipes and that:

the modified cigarettes should be 10 times less toxic than conventional cigarettes and should not represent a health hazard.

It is important to note even if a filter were produced which could remove all of the coloured hydrocarbons or tar from the smoke it would not be possible to claim that the smoke represented no health hazard or even that it was "safer". Until all of the potentially hazardous components and groups of components are discovered (a very formidable undertaking) the only method of producing a "safe" cigarette is to correct the combustion variables, which are responsible for producing the hazardous substances, so that they are similar to those of a known safe method of smoking. From thermodynamic considerations it is then possible to claim that such an altered cigarette would be "safe".

100086669

References

- (1) U. S. A. Public Health Service Publication #1103
Advisory Committee to the Surgeon General on
Smoking and Health.
- (2) E. C. Hammond National Cancer Institute Mono-
graph No. 19 P. 127-204. 1966. Smoking in
Relation to the Death Rates of One Million Men
and Women.
- (3) E. C. Hammond Journal of the National Cancer
Institute Vol. 32, No. 5, May 1964. Smoking in
Relation to Mortality and Morbidity.
- (4) E. C. Hammond, and L. Garfinkel National Cancer
Insitiute Monograph No. 19, P. 269-285, 1966.
- (5) G. P. Tauey, & R. C. Mumpowder Tobacco
Vol. 144, No. 8, PP. 18-22, 1957.

100086670