

The Thermal Degradation of Tobacco

VI. Influence of Extraction on the Formation of Some Major Gas Phase Constituents*

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INTRODUCTION

Recent studies on the thermal decomposition of tobacco showed that the major gas phase constituents are formed at well defined temperatures and their temperatures for maximum formation generally correspond to the temperatures of maximum weight change which occurs between 200°–450° C (1, 2). Furthermore, the extraction of tobacco with various solvents had an influence on the thermal degradation of tobacco and CO and CO₂ formation (1). The objectives of this study were to determine the influence of extraction on the removal of specific gas phase precursors from tobacco and the synergetic or antagonistic effects of the extracted leaf materials on the formation of the gas phase constituents. This has been achieved by determining the formation profiles for methane, ethane, ethene, propane, propene, isoprene, benzene, toluene, formaldehyde, acetaldehyde, acetone, 2-butanone and acetonitrile obtained during the thermal degradation of reference tobacco extracted with hexane, chloroform, acetone, acetonitrile or methanol.

EXPERIMENTAL

The tobacco used for this study was the University of Kentucky 1R1 blend, and the procedures used for its extraction with hexane, chloroform, acetone, acetonitrile and methanol has been described previously (1). The apparatus and conditions employed for the thermal decomposition of tobacco and the analysis of the effluent gas also have been described (1, 2). All thermal analyses were conducted in helium. The volatile products were identified by comparison of the retention time of the unknown peaks with that of authentic compounds and by comparison with retention data from previous studies (2–4). All peaks are plotted

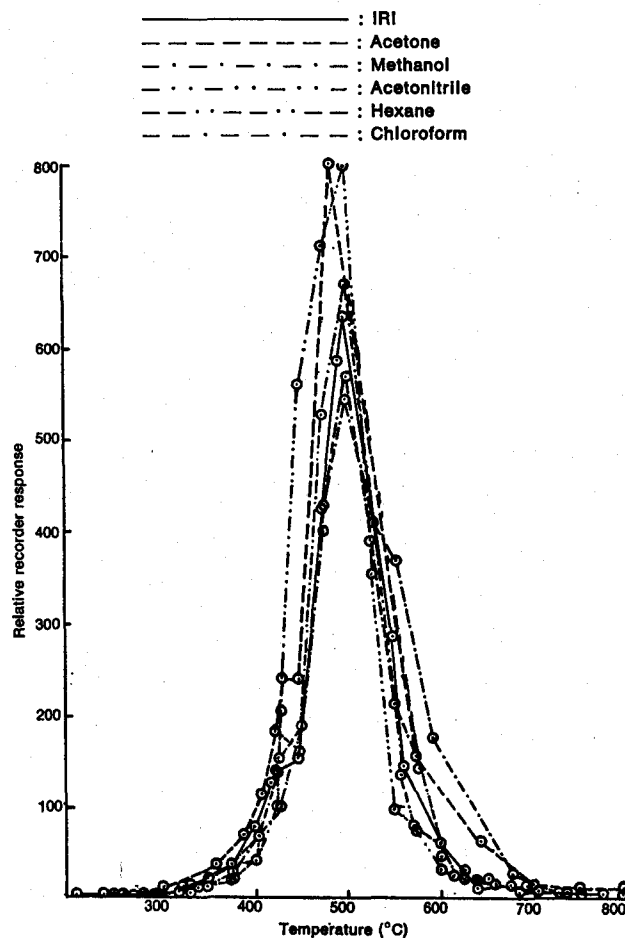
and compared in terms of relative recorder response. The profiles obtained from the non-extracted tobacco are included for comparison with the profiles obtained from the extracted tobaccos.

RESULTS AND DISCUSSION

1. Alkanes and Alkenes

The profiles for methane (Fig. 1) show that the extraction of tobacco did not influence its temperature of maximum formation. From the profiles it appears that extraction of tobacco with polar solvents enhanced

Figure 1. Formation profiles for methane from the thermal degradation of extracted tobaccos.



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methane formation; however, if the sample weights are adjusted to the equivalent weight of the standard blend there would be a slight decrease in the formation of methane. Ethene and ethane profiles from the extracted tobaccos show the same trend even though their temperatures for maximum formation are 50° C lower than those of methane (Figures 2 and 3). Since extraction did not enhance or decrease the formation of these hydrocarbons, the data indicate that the soluble leaf constituents are not the major precursors of methane, ethene, or ethane. This is expected since the major weight loss of the soluble leaf constituents occurs below 400° C (5) and they are not available for thermal degradation during the temperature for maximum hydrocarbon formation. Therefore, the major precursors for these hydrocarbons are those constituents that decompose above 400° C. These would include polymeric components such as partially decomposed carbohydrates, cellulosic materials, lignin, proteins, and brown pigments.

The large differences in the formation profiles for propene (Fig. 4) indicate that propene either has specific leaf precursors or that removal of certain soluble leaf constituents influences its formation. There is no correlation between the amount of leaf material removed and the formation of propene. The formation

profiles obtained from thermal degradation of the tobacco extracts show that propene and propane are formed in disproportionate quantities in contrast to methane, ethane, or ethene (5), which shows that the soluble leaf constituents are good precursors for these two hydrocarbons. The explanation for the anomalous behaviour is beyond the scope of this study. However studies are being continued in order to clearly define the contribution of soluble leaf constituents to the formation of the C₃ hydrocarbons.

The formation profiles for propane also show that extraction of tobacco decreased its level of formation (Fig. 5). Propane profiles were previously shown to contain at least three or more components (2), which explains the presence of the maximum at approximately 250° C. Acetonitrile-extracted tobacco enhanced propane formation, whereas methanol-extracted tobacco decreased propane formation. Profiles obtained for hydrocarbons such as butane and pentane are similar to the above-mentioned profiles with respect to the temperature for maximum formation and the influence of extraction on their levels of formation (5).

The profiles for the saturated and unsaturated hydrocarbons show that extraction does not have a large influence on their temperature for maximum formation. This is further evidence to support the hypothesis that the low molecular weight products are formed from thermal degradation of the nonvolatile carbonaceous residue of the thermally modified tobacco and that, except for propane and propene, the soluble leaf constituents do not contribute disproportionately to hydrocarbon formation. Since the aliphatic hydrocarbons have similar temperatures of maximum formation and the same temperature range for formation, it can be assumed that they are derived during similar decomposition reactions and from similar precursors.

Figure 2. Formation profiles for ethene from the extracted tobaccos.

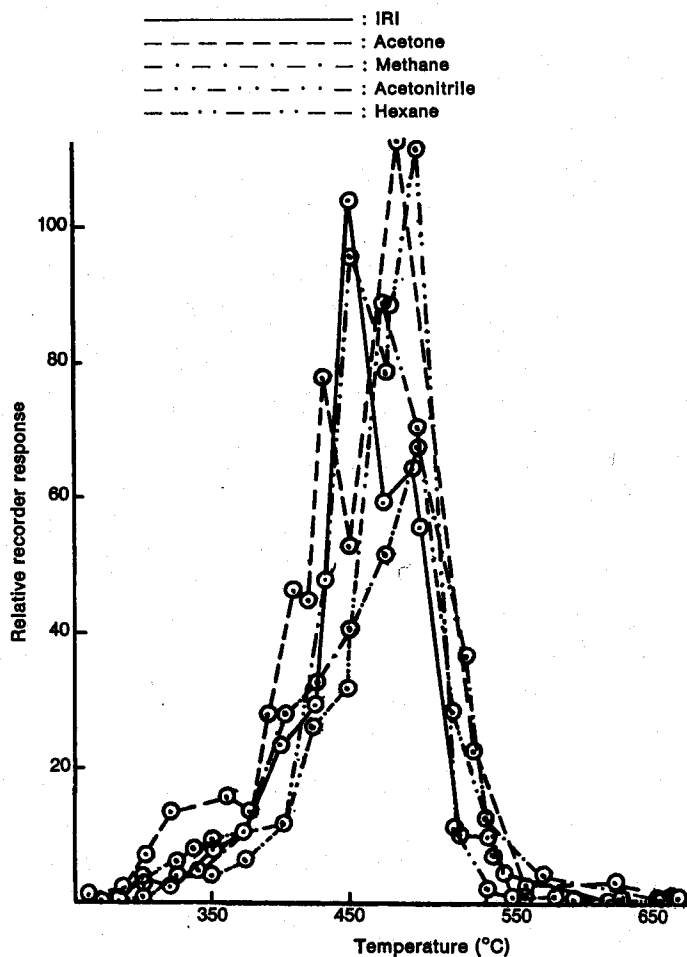


Figure 3. Formation profiles for ethane from the extracted tobaccos.

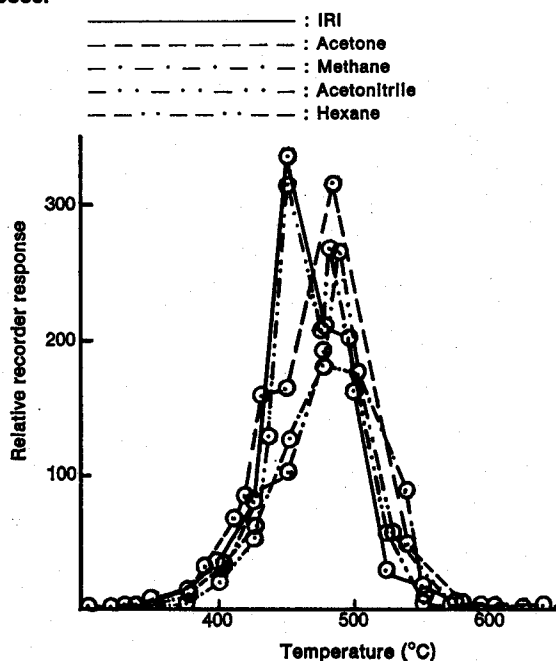


Figure 4. Formation profiles for propene from the extracted tobaccos.

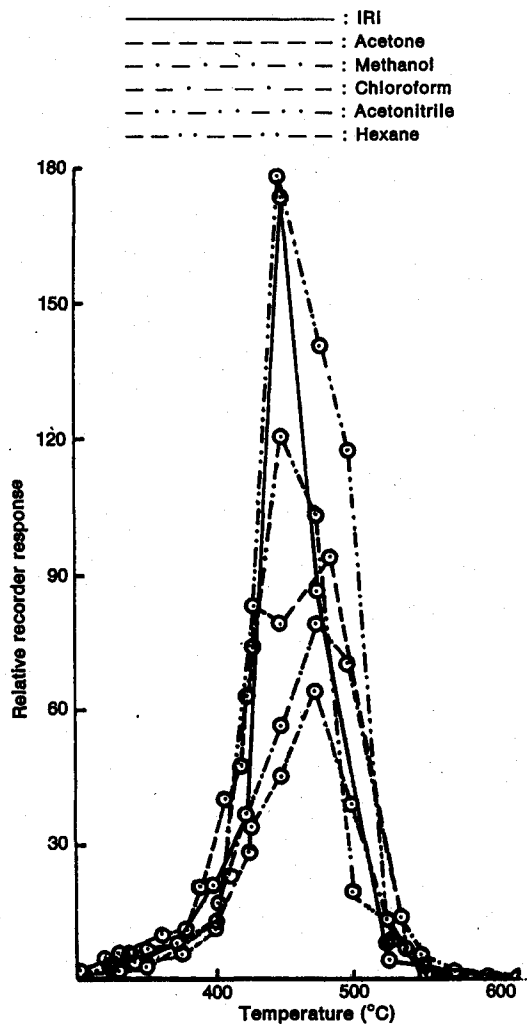
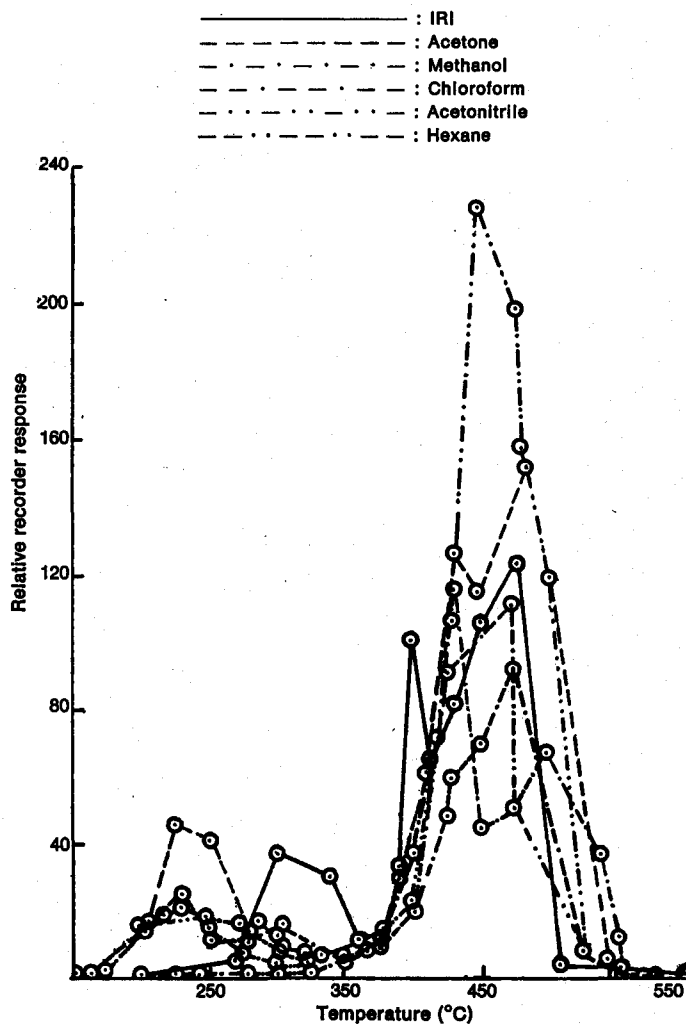


Figure 5. Formation profiles for propane from the extracted tobaccos.



2. Isoprene

The isoprene formation profile is different from those of the aliphatic hydrocarbons since it contains maxima at 375° and 450° C (Fig. 6). Extraction of tobacco with a non-polar solvent, such as hexane, reduced the level of isoprene produced at 375° C. This provides evidence that the maximum at this temperature is due to the decomposition of the non-polar isoprenoid constituents of tobacco. Since the extraction of tobacco with hexane did not reduce the maximum at 450° C, the thermal decomposition of the more polar isoprenoids most likely is responsible for this formation maximum. This conclusion is supported by the profiles obtained from methanol- und acetone-extracted tobaccos which have reduced maxima at both 375° and 450° C. Pyrolysis gas chromatography (PGC) profiles more

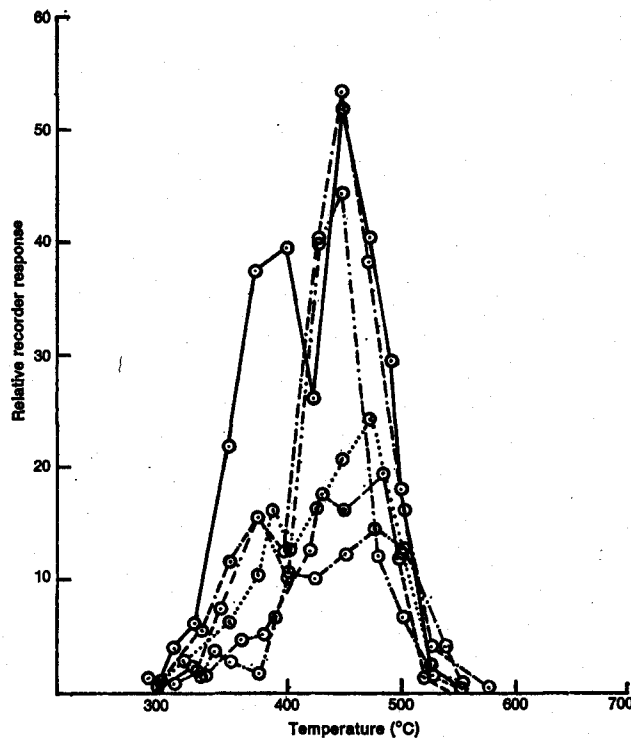


Figure 6. Formation profiles for isoprene from the thermal degradation of extracted tobaccos.

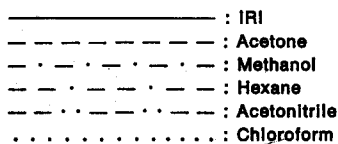
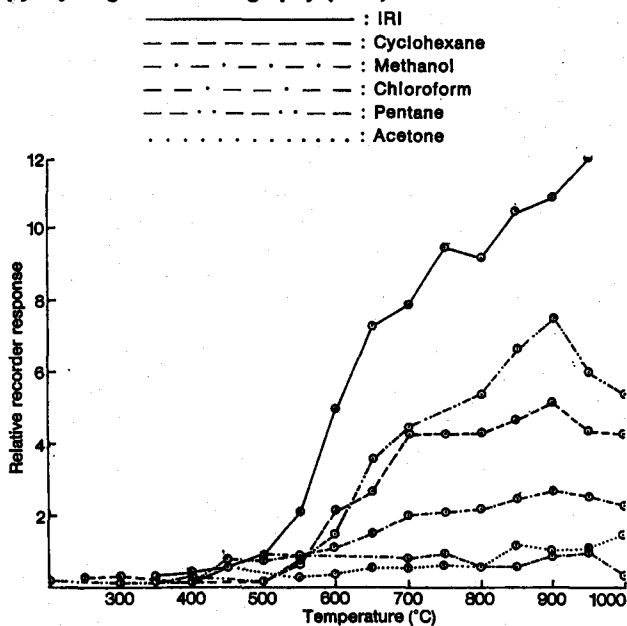


Figure 7. Temperature-yield profiles of isoprene from the pyrolysis gas chromatography (PGC) of extracted tobaccos.



vividly show the influence of extraction on the removal of the isoprene precursors (Fig. 7). There is an inverse relationship between the polarity of the extraction solvent and the level of isoprene that was formed during pyrolysis. These PGC profiles also show that during static thermal decomposition of tobacco the temperature for maximum formation (recovery) is at approximately 900° C, which is 450° C higher than the profiles obtained from dynamic thermal analysis of tobacco. This would be expected since during static conditions the complete tobacco sample is pyrolyzed at a single temperature and at higher temperatures many leaf constituents, which would otherwise volatilize under less severe thermal conditions, undergo thermal decomposition.

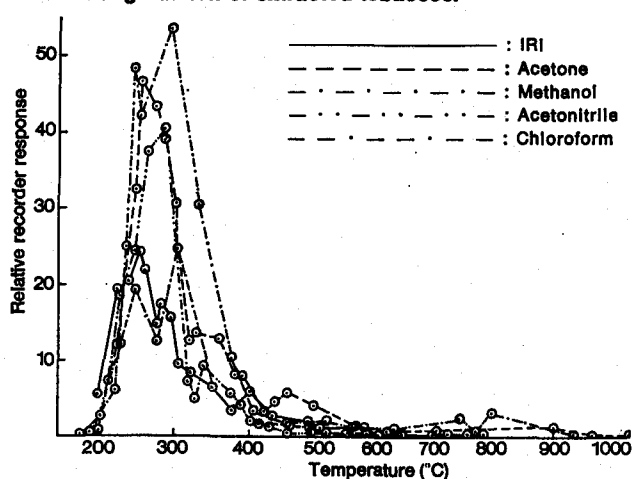
The formation profiles obtained from these extracted tobaccos agree with smoke data from another study (6). The smoke from ether-extracted cigarettes have reduced isoprene levels and the smoke from methanol-extracted cigarettes contains even lower levels of isoprene in the gas phase. Data from this laboratory also show the same trend (5). These data conclusively show that the major precursors of isoprene are the soluble leaf constituents and, therefore, they can be conveniently removed from tobacco by solvent extraction.

3. Aldehydes and Ketones

Extraction of tobacco did not influence the temperature for maximum formation of formaldehyde (Fig. 8), but it did effect an increase in the amount formed. Extraction gave greater than a twofold increase in formaldehyde formation, yet the amount of soluble leaf constituents that have been removed is less than 40% of the dry weight of tobacco. This indicates that the soluble leaf constituents have an antagonistic influence on formaldehyde formation.

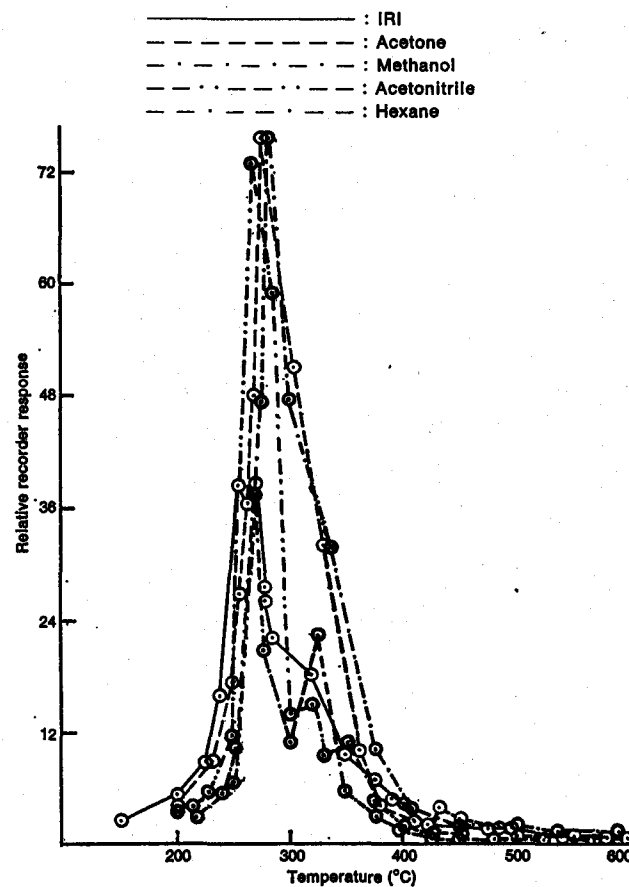
The profiles for acetaldehyde (Fig. 9) also show that

Figure 8. Formation profiles for formaldehyde from the thermal degradation of extracted tobaccos.



extraction of tobacco did not shift the temperature for maximum formation, yet there was an increase in acetaldehyde formation. Again, the soluble leaf constituents have an antagonistic influence on the formation of the low molecular weight aldehydes. This observation is also supported by smoke analysis data (6) which showed that the level of acetaldehyde in the gas phase of smoke from tobacco extracted with either ether or methanol was higher than the level of acetaldehyde in the smoke from the non-extracted tobacco. These pyrolysis data and smoke data indicate that the

Figure 9. Formation profiles for acetaldehyde from the thermal degradation of extracted tobaccos.

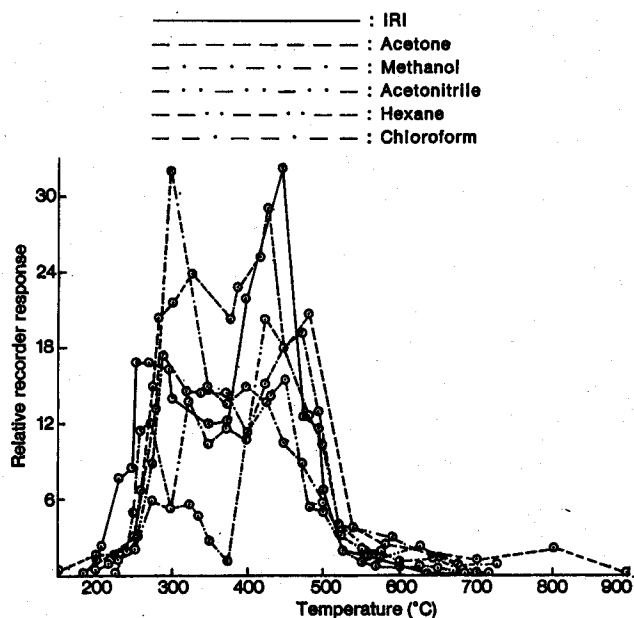


lower levels of acetaldehyde formed from non-extracted tobacco is due mainly to the interaction of the soluble leaf constituents with acetaldehyde or its precursors, such as the carbohydrates, rather than to the alteration of the burn characteristics of tobacco.

The formation profiles (Fig. 10) from the extracted tobaccos show that there are two regions for maximum formation of acetone. Only methanol-, acetone-, and chloroform-extracted tobaccos show enhanced acetone formation. The apparent increase in acetone formation at low temperatures from acetone-extracted tobacco is most likely due to solvent absorption. All acetone profiles show that its major formation is at approximately 450° C, which agrees with the profile obtained from the non-extracted tobacco. As noted earlier (2), the acetone profile contains at least four additional unresolved components: acrolein, propionaldehyde, furan and propionitrile. Since the level of these components constitutes less than 50 percent of the total amount of acetone found in cigarette smoke (7), this profile has been designated as acetone.

The profiles for 2-butanone are similar to those of acetone since they contain two defined areas for maximum formation (Fig. 11). 2-Butanone is formed in lower quantities than acetone, which is in agreement with published smoke analytical data (7). Extraction affects 2-butanone formation, but these data show no specific trend with regard to its level of formation and the amount of soluble leaf constituents removed by extraction. However, in comparison with the non-extracted tobacco, the extraction of tobacco with methanol reduces 2-butanone formation at 275° C, whereas, with chloroform, methanol, and acetonitrile its formation is reduced between 400° and 500° C. The 2-butanone profile contains at least one additional component, that of 2-methyl-propionaldehyde (2). However, the latter constitutes less than 25% of the

Figure 11. Formation profiles for 2-butanone from the thermal degradation of extracted tobaccos.



total amount of 2-butanone that is formed. The apparent increase of 2-butanone formation at lower temperatures from chloroform-extracted tobacco may be due to the volatilization of absorbed chloroform from tobacco. It should be noted that under the described chromatographic conditions (2) chloroform and 2-butanone have the same retention times on the Poropak Q column. Therefore, the profile for 2-butanone from CHCl_3 -extracted tobacco should be disregarded at temperatures below 350° C.

The data for the formation of these ketones are not as definitive as those obtained for the aldehydes. This may be due in part to contamination by the other pyrolysis products. It is also possible that the ex-

Figure 10. Formation profiles for acetone from the thermal degradation of extracted tobaccos.

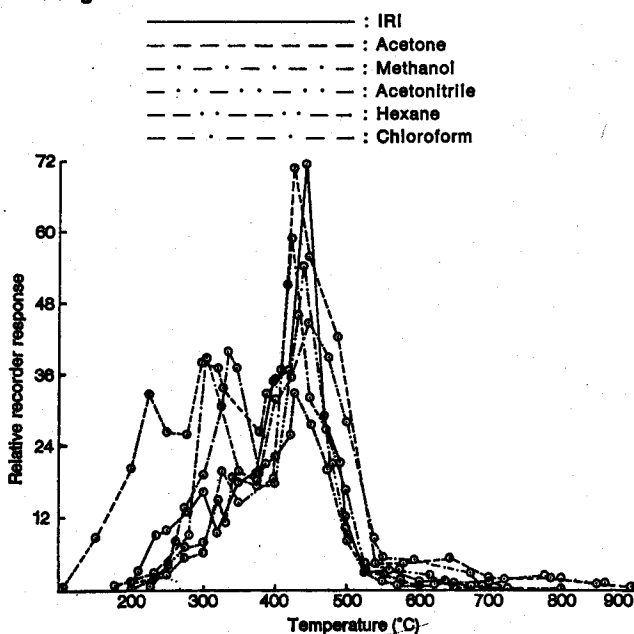
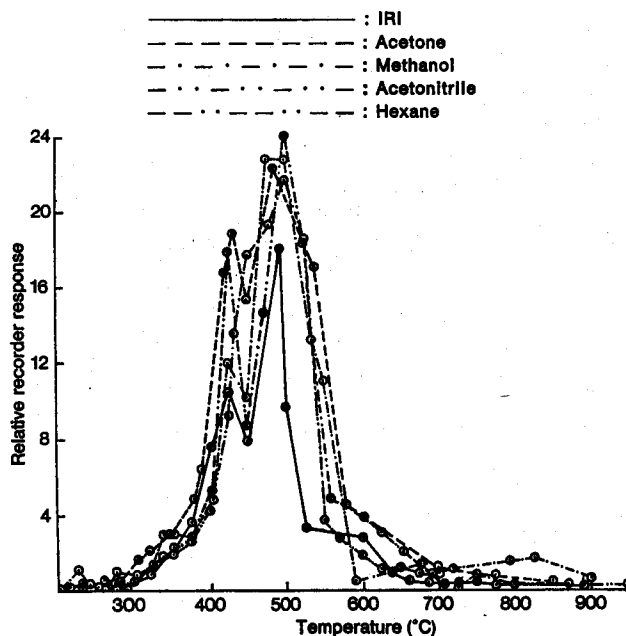


Figure 12. Formation profiles for acetonitrile from the thermal degradation of extracted tobaccos.



traction of tobacco has no major influence on the formation of these ketones. Gas phase analysis of the smoke from cigarettes made from extracted tobacco show that extraction has no influence on the level of either acetone or 2-butanone (6).

4. Acetonitrile

The formation profiles for acetonitrile contain two formation maxima which are centered at 410° C and approximately 500° C (Fig. 12). This is of particular interest since it shows that there are two specific thermal regions involving optimum acetonitrile pyro-synthesis and indicates that at least two types of precursors are involved in its synthesis. Extraction increases acetonitrile formation especially at 410° C. This is expected since extraction of tobacco with organic solvents increases the relative weight percent of the nitrogenous components of the extracted leaf, especially, in the case of methanol-extracted tobacco (6).

Acetonitrile is important not only because it is one of the major nitrogenous hydrocarbons in the gas phase, but its profile defines the thermal environment required for decomposition of the nitrogenous leaf constituents. Even though proteins, amino acids, and other alkaloids undergo decomposition or volatilization at 250° C these profiles show that low temperatures of thermal degradation do not contribute significantly to acetonitrile formation. However, when the temperature of the tobacco substrate is increased to 400° C the acetonitrile formation is favored. This observation supports published data on the pyrolysis of both proteins and amino acids (8, 9).

5. Benzene and Toluene

In comparison with the reference tobacco, extraction of tobacco did not shift the temperature of maximum

Figure 13. Formation profiles for benzene from the thermal degradation of extracted tobaccos.

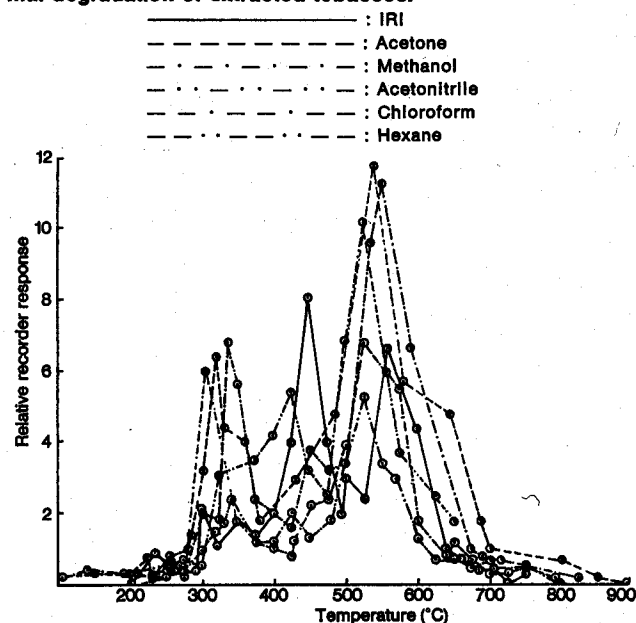
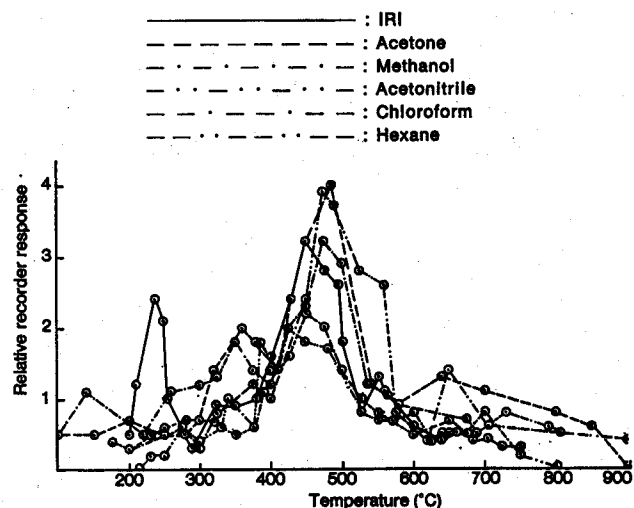


Figure 14. Formation profiles for toluene from the thermal degradation of extracted tobaccos.



formation for benzene (Fig. 13); however, it did effect an increase in benzene formation at lower temperatures (200°-350° C). These profiles show that during the thermal decomposition of tobacco there are at least two temperature regions for the maximum formation of benzene. The temperature maximum shows that benzene is formed in small quantities during the major weight loss of tobacco. Therefore, it can be formed in a burning cigarette at these temperatures even though the major portion of it is formed between 450° and 600° C.

Toluene's formation (Fig. 14) is similar to benzene since it also has two maxima (Fig. 14). However, the maximum at 450° C is 100° C lower than the corresponding maximum of benzene. Extraction does not have a significant influence on toluene formation which is in agreement with smoke data from extracted cigarettes (6). It also should be noted that the data for benzene from our study also agree with the smoke data from extracted cigarettes which shows that extraction had no influence on the levels of either toluene or benzene in the gas phase (6). Since there is agreement between smoke data and the data from the thermal decomposition of tobacco, it is apparent that the latter method can be useful for studying the effects of product modification on the formation temperatures of the gas phase constituents.

SUMMARY

Formation profiles have been determined for the major gas phase constituents formed in an inert atmosphere during the dynamic thermal decomposition of tobaccos extracted with hexane, chloroform, acetone, acetonitrile, and methanol. The profiles include methane, ethane, ethene, propane, propene, isoprene, formaldehyde, acetaldehyde, acetone, 2-butanone, acetonitrile, benzene, and toluene. Except for propene and propane, extraction of tobacco does not dramatically influence

either the temperatures for maximum formation or the level of hydrocarbons formed during thermal decomposition of the tobaccos. This suggests that the majority of the gas phase hydrocarbons are formed from the insoluble leaf constituents. Isoprene has formation maxima at 375° C and 450° C, and extraction of tobacco with non-polar solvents removes leaf precursors responsible for the formation maxima at 375° C. Polar solvents remove the major isoprene precursors which are responsible for the maxima at 375° and 450° C. Extraction effects an increase of both formaldehyde and acetaldehyde formation but has little influence on the formation of either acetone or 2-butanone. The formation profile for acetonitrile has been established and shows that it has maximum formation at 410° and 500° C. Extraction has no influence either on the formation of benzene or toluene. Data from the profiles of these volatile constituents generally agree with smoke data from extracted tobacco which indicates that this method is useful for studying factors that influence the formation of the gas phase constituents.

ZUSAMMENFASSUNG

Es werden Entstehungsprofile dargestellt für die hauptsächlichsten Inhaltsstoffe der Gasphase, die sich in einer inerten Atmosphäre während der dynamischen thermischen Zersetzung von Tabaken bilden, welche mit Hexan, Chloroform, Aceton, Acetonitril und Methanol extrahiert wurden. Es handelt sich um folgende Verbindungen: Methan, Äthan, Äthen, Propan, Propen, Isopren, Formaldehyd, Acetaldehyd, Aceton, 2-Butanon, Acetonitril, Benzol und Toluol. Die Extraktion des Tabaks übt außer bei Propen und Propan weder auf die Temperatur des Bildungsmaximums noch auf die Menge an Kohlenwasserstoffen, die während der thermischen Zersetzung der Tabake entstehen, einen wesentlichen Einfluß aus. Dies legt den Schluß nahe, daß sich die Mehrzahl der Kohlenwasserstoffe der Gasphase aus den unlöslichen Blattbestandteilen bildet. Die Entstehungsmaxima von Isopren liegen bei 375° und 450° C, und durch die Extraktion des Tabaks mit nichtpolaren Lösungsmitteln werden die im Blatt enthaltenen Vorläufer der Verbindung, auf die das Maximum bei 375° C zurückzuführen ist, entfernt. Durch polare Lösungsmittel werden die hauptsächlichsten Isoprenvorläufer beseitigt, die für die Maxima bei 375° und 450° C verantwortlich sind. Die Extraktion bewirkt eine Zunahme der Bildung von Formaldehyd und Acetaldehyd, hat aber wenig Einfluß auf die Bildung von Aceton und 2-Butanon. Das Bildungsprofil für Acetonitril zeigt, daß diese Verbindung Bildungsmaxima bei 410° und 500° C hat. Auf die Bildung von Benzol und Toluol übt die Extraktion keinen Einfluß aus. Werte aus den Profilen dieser flüchtigen Inhaltsstoffe stimmen im allgemeinen mit den Daten für Rauch aus extrahiertem Tabak überein, was zeigt, daß diese Methode für die Untersuchung der Faktoren, die die Bildung der Gasphasenbestandteile beeinflussen, geeignet ist.

RESUME

On a déterminé les courbes de formation des constituants majeurs de la phase gazeuse, produits dans une atmosphère inerte durant la décomposition thermique dynamique de tabacs extraits préalablement à l'hexane, le chloroforme, l'acétone, l'acétonitrile et le méthanol. Les profils traitent du méthane, éthane, éthène, propane, propène, isoprène, de la formaldéhyde, l'acétaldéhyde, l'acétone, le 2-butanone, l'acétonitrile, du benzène et du toluène. A l'exception du propène et du propane, l'extraction préalable du tabac n'affecte pas considérablement les températures de formation maximale ni la quantité d'hydrocarbures produits durant la décomposition thermique des tabacs. Ceci suggère que la majorité des hydrocarbures de la phase gazeuse sont formés à partir des constituants insolubles présents dans la feuille. L'isoprène a une formation maximale à 375° C et 450° C, et l'extraction du tabac avec des solvants non polaires élimine de la feuille les précurseurs responsables du maximum de 375° C. L'extraction avec des solvants polaires élimine les principaux précurseurs de l'isoprène produisant les maxima à 375° C et 450° C. L'extraction provoque une formation plus importante d'acétaldéhyde et de formaldéhyde, mais a peu d'influence sur la formation d'acétone ou de 2-butanone. La courbe de formation de l'acétonitrile a été établie et montre des maxima à 410° C et 500° C. L'extraction n'a pas d'influence sur la formation du benzène et du toluène. Les données obtenues par ces courbes concordent en général avec les données obtenues en fumant des tabacs extraits. Ceci indique que la méthode est utile pour l'étude des facteurs influençant la formation des constituants de la phase gazeuse.

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