

Fundamental Studies on Combustion of Solid Propellants

Part I. Pyrolysis of a Polymeric Fuel Binder

Masao Nagao* and Tsutomu Hikita**

I. Introduction

Studies on combustion of solid rocket propellants are classified into a number of fields. In this research, a fundamental combustion mechanism was investigated experimentally. The initial step in a series of reactions occurring during propellant combustion is conversion of solid constituents to reactive gases. On this problem F. Daniels presented a hypothesis concerning rate-determining step and burning rate of double-base propellants.¹⁾ By using an Arrhenius type regression rate equation he obtained 46.7 kcal/mole for an activation energy of N-O bond from his experimental results, and evaluated burning-rates theoretically. However, this treatment was lacking in pressure dependence of burning rates. Schultz et al. developed this way of reasoning to burning of composite solid propellants and proposed a two temperature theory.^{2,3)} And these macroscopic treatments of polymer degradation processes have been developed into a microscopic analysis by B. Ravinovitch.⁴⁾

In addition to pyrolysis reaction of polymeric binders, the burning processes of composite solid propellants involve heat and mass transfer by laminar and turbulent diffusion and a number of gas-phase chain reactions. Rice⁵⁾ and Geckler⁶⁾ emphasized that the time required for mixing by diffusion of the gase-

ous fuel and oxidizer streams, should be taken into consideration of the overall conversion rate and might be of dominant importance unless melting of surface and liquid phase mixing would precede gasification. This diffusion model led to the conclusion that the burning rate was unaffected by pressure, which was incorrect. M. Summerfield⁷⁾ presented a theory of burning that yielded certain predictions regarding effects of pressure, fuel-oxidant ratio, particle size and burning rate catalyst contents. Summerfield's theory was epoch-making in that the pressure exponent was derived theoretically which fairly agreed with experimental results. However, this theory fails to offer directions for controlling pressure exponents in order to obtain mesa- or plateau-burning. And neither does it explain the difference between a pressure exponent of ammonium perchlorate and that of potassium perchlorate propellants. These disadvantages might be resulted from the fact that his treatment was not chemical but mechanical.

An ideal theory should be such one that makes possible (1) control of a burning rate, (2) establishment of mesa- or plateau-burning, (3) selection of catalysts and oxidants, and so on. Unfortunately, there does not exist any dependable theory to guide propellant formulations at present. This is due to lack of investigations based upon chemical reaction mechanisms and kinetics.

After pyrolysis of solid phase of propellants, reactions take place in the gaseous phase.

* At present, Asahi Kasei Co., Ltd., Sakanoichi Plant, Ohita.

** Lab. of Combustion, Faculty of Engg., Univ. of Tokyo, Bunkyo-ku, Tokyo.

Reactions of ammonium perchlorate were investigated by Levy and Friedman,¹⁰⁾ and many others, those of composite propellants by M. Summerfield,^{7) 8) 9)} L. A. Povinelli,¹¹⁾ S. Tsuchiya¹²⁾ and so on. However, investigations of gaseous reactions were limited to measurements of flame temperatures, analysis of combustion products and intensity measurements of spectral lines. Only S. Tsuchiya referred to a reaction mechanism by comparison of theoretical and experimental values of flame temperatures. And a conclusion was derived that the chemical equilibrium was not attained in the flame gas of ammonium perchlorate propellants, and that this chemically non-equilibrium state was due to existence of excess nitric oxide produced by thermal decomposition of ammonium perchlorate. Although many investigations have been reported of combustion mechanisms and kinetics, experiments have scarcely been carried out with gaseous reactions during combustion of composite propellants except one which McD. Cummings¹³⁾ reported recently.

As reviewed, informations about chemical reactions in propellant combustion are so meager that a theory cannot be developed which would combine propellant combustion to chemical reactions incorporated therein. Therefore this program was designed in order to obtain more basic informations. Pyrolysis of a polymeric fuel binder was experimentally investigated for the first step.

Studies on kinetics and mechanisms of polymer degradation have been conducted by specialists in high polymer chemistry, whose main objects are in elucidation of chemical structures of natural materials, understanding of processes in breakdown, getting informations about the structure and composition of copolymers and so on. Therefore those experiments have been carried out under mild

conditions, i. e., energy is small which is supplied to polymers for degradation. In combustion of solid propellants, polymeric binders are exposed to the heat flux of high intensity. For establishment of such an experimental condition, an apparatus was developed which was equipped with an intense heating element. Analyses of degradation products have been reported of double-base propellants¹⁴⁾ and ammonium perchlorate,¹⁵⁾ but not of polymeric fuel components of composite propellants.

A great number of papers have been presented regarding degradation reactions of polymethyl methacrylate and polystyrene. A few informations, however, can be found in literatures with respect to pyrolysis of polybutadiene which was used as a sample in this program. Samsel¹⁶⁾ and Cobler obtained gas chromatograms of pyrolyzates of polybutadiene but did not identify them. Volatile degradation products of polybutadiene were analyzed by Wall.¹⁷⁾ These products, shown in Table 1, formed three per cent of the original sample heated to 400°C. The monomer yield from polybutadiene amounted to one per cent. Madorsky and coworkers¹⁸⁾ carried out a more detailed analysis. Pyrolysis in vacuum produced two main fractions, volatile and involatile at room temperature. The latter constituted at least 80~90 per cent of the whole, and the average molecular weight was 739, which meant that on the average fragments in this fraction consisted of about 13~14 monomer units. Two main components of volatile fractions were butadiene and butenes. These were analyzed by means of a mass spectrometer. Analyses of pyrolyzates of polybutadiene are tabulated in Table 1. In our research, effects were studied of pyrolysis temperatures and contact time on amount of pyrolyzates. In addition, dissociation energies of C-C bonds in the long chain of polybuta-

Table 1 Pyrolyzates of Polybutadiene

Investigator	The authors	Madorsky	Wall
Method of Analysis	Gas chro.	Mass spec.	?
Pyrolysis Temperature	450~1000	350~500	400
Component/Pressure	1 atm	in vacuum	1 atm
Hydrogen	D	—	D
Methane	D	—	—
Acetylene	D	—	—
Ethylene	D	D	—
Ethane	D	D	D
Propadiene	—	D	—
Propylene	—	D	D
Propane	—	D	D
1,3-Butadiene	D	D	D
Butenes	—	D	—
Butanes	—	D	—
Cyclopentadienes	—	D	—
Pentadienes	—	D	—
Pentenes	—	D	D
Pentanes	—	D	D
Benzene	—	—	D
Cyclohexadienes	—	D	—
Cyclohexene	—	—	D
Hexadienes	—	D	D
Hexenes	—	D	—
Vinylcyclohexene	D	D	D
Unknown compound (B. p. >200°C)	D	*	—

D: Detected,
 —: Not detected,
 *: Detected, but not by a mass spectrometer.

diene were estimated and a pyrolysis mechanism was speculated.

II. Experimental Apparatus and Procedure

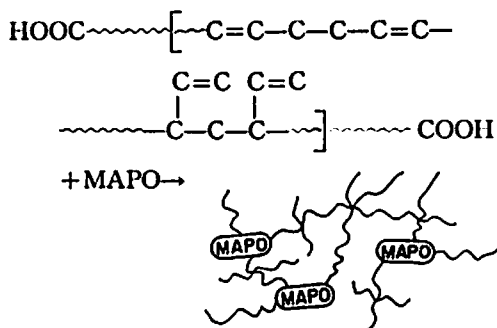
A pyrolysis chamber consists essentially of a 17 mm. transparent silica tube heated with a cylindrical heating element. The furnace, which is controlled by a variable transformer to raise the temperature up to 1,300°C. A sample rod has a short pin at the head end, with which a piece of sample is stabbed and inserted rapidly into the center of the chamber at a desired temperature.

For analysis of pyrolysis products, the gas chromatograph of Yanagimoto GCG 220 employing thermal conductivity detectors was used. Light gasses except methane and hydrogen were sampled in a trap cooled with liquid nitrogen. Compounds with high boiling points were injected directly into gas chromatography in the manner employed in pyrolysis gas chromatography technique. Methan and hydrogen were trapped in a gas sampling vessel, and analyzed qualitatively. Gas chromatographic conditions employed are shown in Table 2.

Table 2 Gas chromatographic conditions

Column No.	Column	Temperature	Gases Analyzed.
1	Di-2-ethyl hexyl sebacate 20% on firebrick (30~60mesh), 2m.	140°C	Vinylcyclohexene Unknown compd.
2	Polydiethylene glycol succinate 25% on Diasolid M, 4m.	25~30	Butadiene-1,3
3	Silica gel, 2m.	"	Acetylene, Ethylene, Ethane, Methane
4	Active Carbon, 3m.	"	Hydrogen, Methane

A thermosetting polymer was used as a sample, the main component of which was polybutadiene (molecular weight=3,770) with carboxyl groups at both ends and which was cured with MAPO. The curing reaction and structure of the polymer are as follows:



III. Experimental Results

Componets of pyrolyzates obtained consisted of:

Hydrogen	Ethane
Methane	Butadiene-1,3
Acetylene	Vinylcyclohexene (a dimer of butadiene-1,3)
Ethylene	Unknown (B. p. >200°C)

These components were completely the same as those obtained in pyrolyzing butadiene-1,3 with an exception of unknown compounds detected on the colum No. 1. The effect of pyrolysis temperature on the amount of each component of pyrolyzates was clearly obtained as illustrated in Figures 1~3. The amount of butadiene monomer reached a maimum value, 5.2 weight per cent of the original polymer, at about 650°C and ethylene 20.8 weight per cent at 800°C when the contact time was 38.6 sec. At lower temperature, the amounts of butadiene

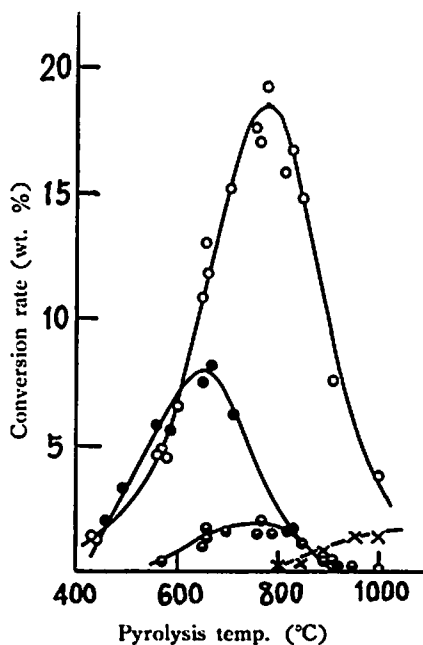


Fig. 2 Effect of pyrolysis temperature on amount of pyrolyzates of polybutadiene (II) Contact time: 26.8sec.

○ Ethylene, ● Butadiene,
◐ Ethane, × Acetylene

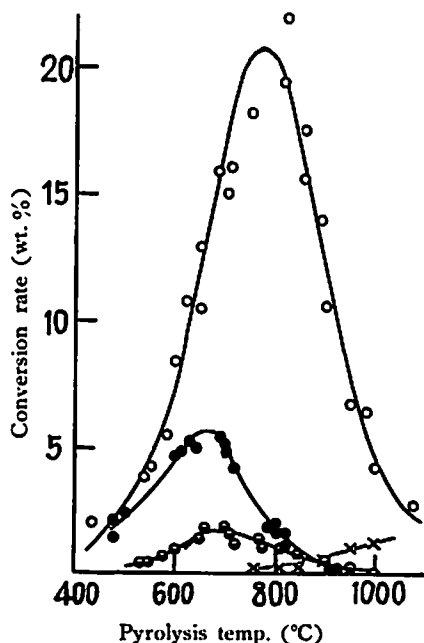


Fig. 1 Effect of pyrolysis temperature on amount of pyrolyzates of polybutadiene (I) Contact time: 38.6 sec.

○ Ethylene, ● Butadiene,
◐ Ethane, × Acetylene

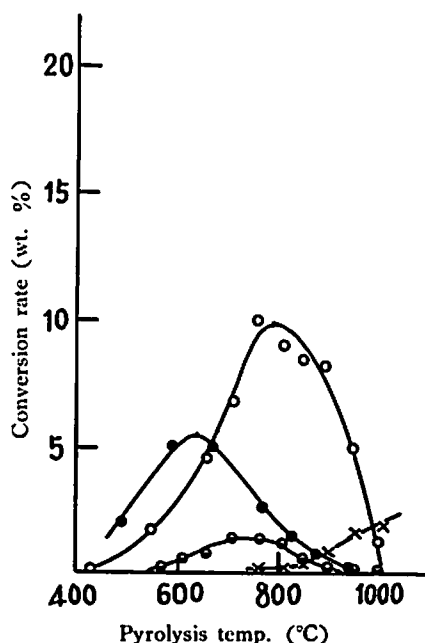


Fig. 3 Effect of pyrolysis temperature on amount of dyrolyzates of polybutadiene (III) Contact time: 13.4sec.

○ Ethylene, ● Butadiene,
◐ Ethane, × Acetylene

and ethylene increase as the degradation temperature is raised. This implies that the primary decomposition (dimer and monomer formation) and secondary decomposition (from butadiene to ethylene and other smaller fragments) take place at the same time and consecutively. The primary decomposition predominates over the secondary decomposition at lower temperatures. At higher temperatures than 650°C, the secondary decomposition predominates and above 800°C, further decomposition takes place. The same behavior of the secondary decomposition can be seen in pyrolysis of butadiene monomer as shown in Figure 4. The maximum yield varied with the flow rate of the carrier gas, but the temperature at which it was attained was kept constant at 650°C for butadiene monomer and 800°C for ethylene.

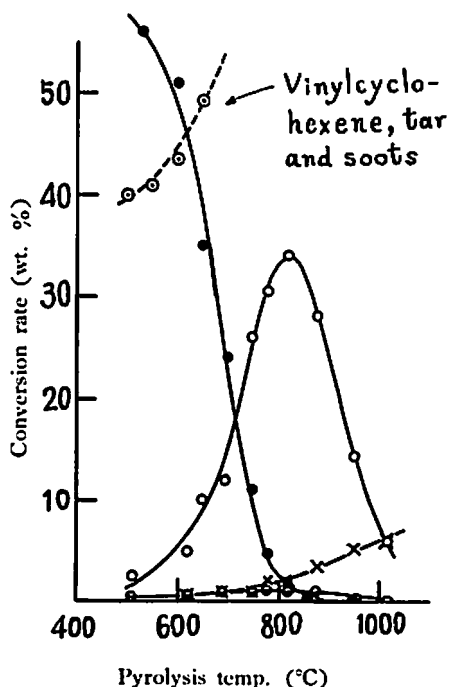


Fig. 4 Temperature effect on pyrolyzates of butadiene monomer.

○ Ethylene, ● Butadiene,
● Ethane, × Acetylene

Variation of flow rates of the carrier gas altered the composition and amount of degradation products. Conversion rate versus contact time is plotted in Figure 5. (The contact time was calculated from the flow rate of the carrier gas.) When the contact time is long, the primary products are not rapidly carried away from the hot zone and secondary reactions take place. When the contact time was 26.8 sec., the conversion rate to butadiene monomer reached a maximum value of 7.8 weight per cent of the original polymer.

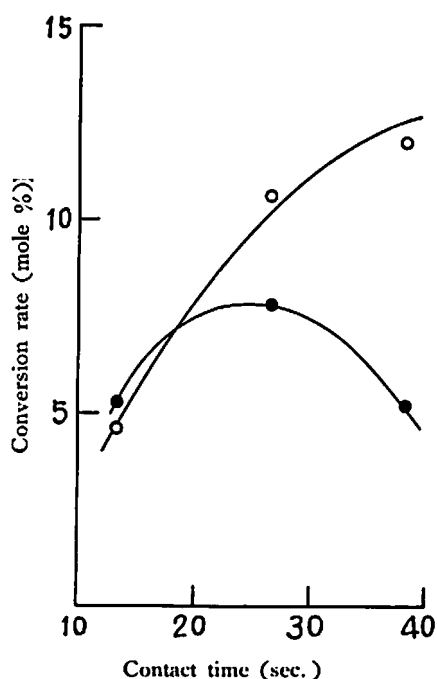


Fig. 5 Effect of contact time on conversion rate to ethylene and butadiene-1,3 (Pyr. Temp. = 650°C)
○ Ethylene, ● Butadiene

IV. Discussion

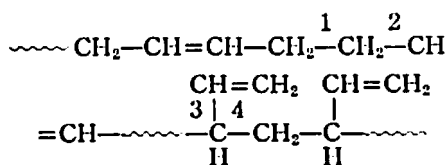
Estimation of Dissociation Energies of C-C bonds:

According to Vedenev,^{(10) (20)} a bond dissociation energy, Q_{R-X} , is empirically represented as

$$Q_{R-X} = E'_{R-X} - (B_R + B_X) \quad (1)$$

where E_{R-X} is an inherent dissociation energy of the $R-X$ bond, and B_R and B_X energies stabilized by radicals R and X respectively. Numerical values of E' and those necessary for calculation of B , are given in literatures.

The main structure of polybutadiene may be illustrated as follows.



Dissociation energies of bond 1, 2, 3, and 4 can be estimated as;

Bond	Dissociation Energy (kcal/mole)
1	41.9
2	81.8
3	85.1
4	62.1

Therefore, it is expected that polybutadiene will decompose at β positions to double bonds, in other words, into monomers, dimers and so on. This has been confirmed by our experiments.

In pyrolysis of polybutadiene, the amount of butadiene monomer increases at first with increasing contact time, and decreases after reaching its maximum value. The former may be attributed to the fact that the polymer decomposes into butadiene dimers, oligomers and so on as well as into monomers. This implies that polybutadiene will decompose in the manner of so-called random chain scission. The latter results from the secondary decomposition of monomers into ethylene and other smaller fragments.

Surface temperature of a propellant during combustion:

G. M. Brauer²¹⁾ obtained that styrene monomer reached a maximum value at 725°C in pyrolysis of polystyrene. M. Summerfield

and co-workers²²⁾ measured surface temperatures of propellants during combustion by using fine thermocouples embedded in solid-propellants. As a surface temperature, about 600°C was obtained for PBAA-AP composite propellants regardless of pressures. According to these facts together with our experimental results, temperatures ranging from 600 to 700 degree might be specified as characteristic temperatures in pyrolysis of polymers. Daniels and other investigators presented and utilized Arrhenius type equations for regression rate of polymers in pyrolysis studies by using a hot plate technique. According to an equation of this type, the surface temperature will exceed 1,000°C under pressures as high as 70kg/cm², such a high temperature being beyond considerations.

Therefore, it will be more reasonable to consider as follows:

(1) an Arrhenius-type regression rate equation is valid at temperatures lower than the characteristic pyrolysis temperature of a polymeric fuel-binder, and

(2) the regression rate of a fuel binder is estimated as a function of heat flux offered to the burning surface 1-1 a regression rate will increase with increasing heat flux from the gaseous combustion zone, so as to keep constant the surface temperature.

This kind of treatment is also employed in studies on ablation accompanied with combustion.²³⁾ The surface temperature of a double base propellant was also obtained as about 300°C by M. Summerfield.²²⁾ This will be due to nitro groups included. Different kinds of materials will have different surface temperatures. Evidently inflammable materials have lower surface temperatures during their combustion. Hence, it is ineffective to put an inflammable material on the surface of a propellant in order to improve ignitability.²⁴⁾ (Of course, it will be effective if an inflamm-

able material were put on in thickness enough to raise the temperature in the chamber so high as to ignite a propellant.)

V. Summary

In pyrolysis of polybutadiene, ethylene, butadiene monomer, vinylcyclohexene (a butadiene dimer), and many other species were obtained. Monomer and dimer formation was predicted by estimation of bond dissociation energies of the polymer by means of Vedenev's method. The amount of butadiene monomer in pyrolyzates reached a maximum value at pyrolysis temperature 650°C, and that of ethylene at 800°C. According to our experimental results and several investigations reported in literatures, we conclude that temperatures ranging from about 600 to 700 degree are characteristic of pyrolysis of polymers. A regression rate equation of an Arrhenius type is only valid when the surface temperature of degrading polymer is lower than the characteristic pyrolysis temperature. And a polymer burns at the characteristic pyrolysis temperature at a rate determined by the intensity of heat flux supplied from the gaseous combustion zone.

References:

- 1) Wilfong, R. E., S. S. Penner and F. Daniels, *J. Phys. Colloid Chem.*, **54**, p. 863 (1950)
- 2) Schultz, R., L. Green, Jr., and S. S. Penner, *Combustion and Propulsion, Third AGARD Colloquium*, p. 367, Pergamon Press, London, (1958)
- 3) Anderson, W. H., K. W. Bills, E. Mishuck, G. Mow and R. D. Schultz, *Comb. and Flame*, **3**, p. 301 (1959)
- 4) Ravinovitch, B., 10th Symp. on Combustion, p. 1395 (1965)
- 5) Rice, O. K., and R. Ginell, *J. Phys. Colloid Chem.*, **54**, p. 885 (1950)
- 6) Geckler, R., *Selected Combustion Problems I* (AGARD), p. 289, Butterworth Scientific Publications, London (1954)
- 7) Summerfield, M., G. S. Sutherland, M. J. Webb, H. J. Taback and K. P. Hall, Preprint No. 737~58 presented at the ARS 13th Annual Meeting, (1958)
- 8) Bastress, E. K., K. P. Hall and M. Summerfield, ARS Preprint No. 1597~61 presented at Solid Propellant Rocket Conference (1961)
- 9) Hall, K. P., J. Wenograd, R. Cole and M. Summerfield, Unclassified Paper AD 274591 (1962)
- 10) Levy, J. B., and R. Friedmann, 8th Symp. on Combustion, p. 663 (1961)
- 11) Povinelli, L. A., *AIAA J.*, **3**, p. 1593 (1965)
- 12) Tsuchiya, S., *Kogyo Kagaku Zasshi*, **65**, p. 843 (1962)
- 13) Cummings, McD., 10th Symp. on Combustion, p. 1365 (1965)
- 14) Wolfrom, M. L., et al., *J. Am. Chem. Soc.*, **77**, p. 6573 (1955)
- 15) Bircumshaw, L. L., and B. H. Newman, *Proc. Roy. Soc. (London)*, **A (227)**, p. 115, (1954)
- 16) Cobler, J. G., and E. P. Samsel, *SPE Transactions*, 1962, p. 145
- 17) Wall, L. A., *J. Research Natl. Bur. Standards*, **41**, p. 315 (1945)
- 18) Madorsky, S. L., S. Straus, D. Thompson and L. Williamson, *J. Polymer Sci.*, **IV**, p. 629 (1945)
- 19) Semenov, N. N., "Some Problems in Chemical Kinetics and Reactivity", a Japanese translation, p. 40, Iwanami Shoten, Tokyo, (1963)
- 20) Shibazaki, Y., *Kobunshi Bunseki Kenkyu Kondankai Data No.* 55~143 (1965)
- 21) Brauer, G. M., *Anal. Chem.*, **33**, p. 673 (1961)
- 22) Sabadell, A. J., J. Wenograd, and M. Summerfield, *AIAA J.*, **3**, p. 1580 (1965)
- 23) Lundell, J. H., R. M. Wakefield, and J. W. Jones, *AIAA J.*, **3**, p. 2087 (1965)
- 24) Akimitsu, K., Private communication

固体推進薬の燃焼に関する基礎的研究

第1報 高分子燃料兼粘結剤の熱分解

長尾 雅男・疋田 強*

固体推進薬の燃焼速度と圧力の関係についてはこれ迄に数多くの研究が報告されているが、それらは流体力学的取扱いによるものが殆どで、化学反応論的立場からの考察は未だ不足になされたものがない。その結果、燃焼速度及びその圧力指数の制御に対する指針が得られない。そこで著者らはこのような問題の解決を最終目標とし、先ずその為の基礎的実験を行なった。

試料はポリブタジエン(PB)を使用。熱分解装置は円筒形高温発熱体の中に石英管を通じたものを作成し、試料が急激に高温に曝されるように設計した。試料を400~1,100°Cの温度範囲で熱分解させ、分解生成ガスを液体窒素で冷却したサンプリングバルブに捕集してガスクロで分析した。水素及びメタンは定性的に確認、高沸点生成物は熱分解ガスクロマトグラフィー法で定性分析した。その結果、検出された分解生成物は：

- | | |
|----------|--------------|
| 1. 水素 | 2. メタン |
| 3. アセチレン | 4. エチレン |
| 5. エタン | 6. ブタジエン-1,3 |

昭和41年7月18日受理

* 東大工学部燃料工学科

7. ビニルシクロヘキセン(ブタジエン二量体)
8. 未知物質(沸点200°C以上)
9. 媒

である。このうち3~6の生成量に対する熱分解温度及び接触時間の影響は図1~3になった。ブタジエン単量体及びエチレンの生成量は熱分解温度が夫々650°C及び800°Cで最大となり、これは接触時間に無関係に観察された。エチレンの生成量が800°Cで最大となるのはブタジエン単量体の熱分解においても観察された(図4)。PB中のC-C結合の解離エネルギーを半経験式を用いて推定した結果、PBは単量体、二量体……等に無秩序に分解することが予測されたが、これは以上の実験結果によつて確認された。

本実験及び他の研究者らの報告から、600~700°Cという温度は高分子の熱分解において特徴的な温度であり、混成系推進薬の燃焼において高分子燃料はこの程度の温度で分解するものと判断される。その分解速度はこの特徴的熱分解温度のもとで燃焼面における熱収支によつて決定され、従来のアレニウス型の後退速度式は点火から定常燃焼までの過渡的状态にのみ適用されるものと考えられる。

ニュース

Hercules 火薬工場の爆発

Carthage, Mo. にある Hercules の産業火薬工場は先週火災と爆発によつて非常に損害を受けた。荒廃にまで到った火災は火薬庫地帯から起り工場を徹収するだけの余裕があった。早期の報告にも拘らず死亡者数は確認されず183の従業員の内唯1名が重傷したにすぎなかった。工場から20マイルはなれた建物の窓が破壊され、衝撃波は10マイル以上で観測された。数人の市民が破片とこわれたガラスで怪いけがをした。製造作業は中止された。損害の評価

はまだ終っていない。

Chem. Week July 23, 1966 (木村 真)

火薬工場爆発

Mc. Arther, Ohio 近くの火薬工場でダイナマイトが爆発し死者5名を出した。負傷者なし。爆発は Austin Powder Co. 工場の35年の歴史の中で4回あり、これは膠質ダイナマイト製造系統で捏和工室が破壊した。爆発及び損害の原因は圧搾の時に起因されない。工場には200人従事している。

Chemical Engineering 1966.6.20. (木村 真)