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RESEARCH MEMORANDUM

FUNDAMENTAL FLAME VELOCITIES OF PURE HYDROCARBONS

II - ALKADIENES

By Oscar Levine, Edgar L. Wong, and Melvin Gerstein

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SUMMARY

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Data are presented for the fundamental flame velocities of 10 pure alkadienes that have isolated, conjugated, or cumulative double-bond systems. On the basis of this limited amount of data and the flame velocities previously reported, it is concluded that unsaturation changes the flame velocity in the order alkanes < alkenes < alkadienes with isolated double bonds \approx alkadienes with conjugated double bonds < alkadienes with cumulative double bonds \approx alkynes. There were no significant differences in the flame velocities of cis and trans 1,3-pentadiene. The alkadienes, 1,2-pentadiene and 2,3-pentadiene, with different positions of the cumulative double bond in the straight chain, have similar flame velocities. Methyl substitution in a hydrocarbon reduces the flame velocity; the extent of the reduction increases with the degree of unsaturation of the hydrocarbon.

INTRODUCTION

Reference 1 presented fundamental flame-velocity data, obtained by a tube method, for 37 hydrocarbons including normal and branched alkanes, alkenes, and alkynes; as well as cyclohexane and benzene. It was concluded that unsaturation changes the flame velocity in the order: alkanes < alkenes < alkynes, and that branching reduces the flame velocity.

This report extends the self-consistent set of fundamental flame-velocity measurements reported in reference 1 with a series of alkadienes for use in correlations with flame-propagation theories and combustor-performance results.

PROCEDURE

The experimental technique is the same as that described in reference 1. A gaseous combustible mixture of pure hydrocarbon and dried air of known composition was prepared and introduced into an evacuated, pyrex, horizontal, cylindrical flame tube with an inside diameter of 25 millimeters and a length of 57 centimeters. An orifice, 8 millimeters in diameter, was placed at the ignition end of the flame tube. A second orifice, 1.7 millimeters in diameter, was inserted at the opposite end of the tube. A small methyl alcohol flame was the source of ignition.

The linear or spatial observed flame velocity U_o is that velocity component normal to the cross-sectional plane of the flame tube. It is a function of hydrocarbon type and concentration and is dependent on the geometry of the experimental apparatus. It was measured at room temperature and atmospheric pressure by means of two photocells placed at a known distance apart and connected to an electronic timer. The uniformity of flame travel in the part of the flame tube between the two photocells was confirmed by the rotating-drum-camera method reported in reference 1.

The fundamental flame velocity U_f is defined as the velocity component normal to any tangent to the flame surface. It is a function of hydrocarbon type and concentration and is entirely independent of the geometry of the experimental apparatus. It was calculated by the equation (reference 1)

$$U_f = (U_o - U_g)(A_t/A_f) \quad (1)$$

where

U_f fundamental flame velocity

U_o linear flame velocity

U_g gas velocity ahead of flame

A_t cross-sectional area of flame tube

A_f flame surface area

In order to evaluate the gas velocity ahead of the advancing flame, the volumetric rate of flow was determined from motion pictures of the progressive growth of a soap bubble blown from a tube connected

to the flame tube. The volumetric rate of flow divided by the cross-sectional area of the flame tube is a mean value of the gas velocity U_g . An empirical relation between the gas velocity and the linear flame velocity was experimentally established (reference 1) and was used to calculate the gas velocity

$$U_g = 0.236 U_0 - 10.47 \quad (2)$$

The surface area of the flame A_f was determined by photographing the flame and calculating the area from the photographs by the method of Coward and Hartwell as modified by the authors (reference 1). The flame surface area was found to have a constant value for every hydrocarbon type and concentration.

The reproducibility of the experimental procedure was confirmed by the periodic testing of n-pentane during the investigation of the alkadienes. At no time did the linear flame velocity for n-pentane deviate more than 2 percent from its original value (reference 1). At least three determinations of the linear flame velocity were made for each mixture concentration studied. The flame velocities reported herein are average values and have a precision of ± 2 percent.

RESULTS AND DISCUSSION

The flame-velocity data together with the source and estimated purity of all the hydrocarbons considered in this investigation are summarized in table I.

The fundamental flame velocity of three series of hydrocarbons with 4, 5, and 6 carbon atoms in the straight chain is presented as a function of hydrocarbon concentration (expressed as fraction of stoichiometric) in figures 1, 2, and 3, respectively. In general, the maximum flame velocity occurs in mixtures containing 10 to 30 percent excess fuel. In figure 4 the maximum flame velocity for each individual hydrocarbon is cross-plotted from figures 1 to 3 against the number of carbon atoms in the straight chain. Addition of a second double bond to an alkene increases the flame velocity; the extent depends on the molecular weight of the alkene and on whether the resulting alkadiene has an isolated, conjugated, or cumulative double-bond system. The maximum flame velocities of 1,3-butadiene and 1,2-butadiene are approximately 26 and 34 percent greater, respectively, than that of 1-butene (reference 1); the flame velocity of 1,2-butadiene is the same as 1-butyne (reference 1). The maximum flame velocities of cis 1,3-pentadiene, trans 1,3-pentadiene, and

1,4-pentadiene are equal within experimental error and approximately 8 percent greater than that of 1-pentene (reference 1); 2,3-pentadiene, 1,2-pentadiene, and 1-pentyne are about equal and roughly 20 percent greater than that of the 1-pentene. It appears that the effects of geometrical isomerism and the position of the cumulative double bonds in the straight chain are insignificant. The maximum flame velocity for 1,5-hexadiene is approximately 5 percent greater than that of 1-hexene (reference 1).

These results indicate that for a constant number of carbon atoms in a straight-chain aliphatic hydrocarbon, unsaturation changes the flame velocity in the order alkanes < alkenes < alkadienes with isolated double bonds \approx alkadienes with conjugated double bonds < alkadienes with cumulative double bonds \approx alkynes.

The effect of methyl substitution on the flame velocity of 1,3-butadiene is illustrated in figure 5. The maximum fundamental flame velocity occurs in mixtures containing approximately 18 percent excess fuel. The effect of methyl substitution on an alkadiene with a conjugated double bond is compared in figure 6 with the effect of methyl substitution on the corresponding alkene and alkane. The maximum flame velocity for each hydrocarbon is plotted against the number of methyl groups substituted for hydrogen atoms in the parent hydrocarbon. Substitution by one methyl group decreases the maximum flame velocity of 1,3-butadiene approximately 17 percent, and substitution by a second methyl group further decreases the peak velocity 7 percent. Substitution by a methyl group in 1-butene (reference 1) decreases the maximum flame velocity 10 percent, and substitution by two methyl groups in n-butane (reference 1) shows no appreciable effect.

In summary, methyl substitution reduces the flame velocity of the hydrocarbons; the extent of the reduction increases with the degree of unsaturation of the corresponding hydrocarbons.

CONCLUSIONS

From an investigation of the fundamental flame velocities of 37 pure hydrocarbons previously reported and 10 pure alkadienes reported herein it is concluded that:

1. Unsaturation changes the flame velocity in the order alkanes < alkenes < alkadienes with isolated double bonds \approx alkadienes with conjugated double bonds < alkadienes with cumulative double bonds \approx alkynes.

2. There were no significant differences in the flame velocities of cis and trans 1,3-pentadiene.

3. The alkadienes, 1,2-pentadiene and 2,3-pentadiene, with different positions of the cumulative double bond in the straight chain, have similar flame velocities.

4. Methyl substitution in a hydrocarbon reduces the flame velocity; the extent of the reduction increases with the degree of unsaturation of the hydrocarbon.

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Cleveland, Ohio.

REFERENCE

1. Gerstein, Melvin, Levine, Oscar, and Wong, Edgar L.: Fundamental Flame Velocities of Pure Hydrocarbons. I - Alkanes, Alkenes, Alkynes, Benzene, and Cyclohexane. NACA RM E50G24, 1950.

TABLE I - FLAME VELOCITIES OF HYDROCARBONS



Fuel	Source	Estimated purity (percent)	Maximum U_o (cm/sec)	¹ Maximum U_o-U_g (cm/sec)	² Maximum U_f		Fraction of stoichiometric at maximum U_f	Volume percent fuel at maximum U_f
					(cm/sec)	(ft/sec)		
Methane*	M ³	99	84.5	75.0	33.8	1.11	1.05	9.96
Ethane*	P ⁴	99.9	102.8	89.0	40.1	1.32	1.11	6.28
Propane*	P	99	99.5	86.5	39.0	1.28	1.13	4.54
n-Butane*	P	99	96.2	84.0	37.9	1.24	1.12	3.52
n-Pentane*	NACA ⁵	99.3	98.0	85.3	38.5	1.26	1.14	2.92
n-Hexane*	NACA	97	98.0	85.3	38.5	1.26	1.16	2.51
n-Heptane*	NACA	----	98.3	85.6	38.6	1.27	1.20	2.26
2-Methylpropane	P	99	87.5	77.3	34.9	1.15	1.11	3.48
2,2-Dimethylpropane*	P	99	83.0	73.9	33.3	1.09	1.11	2.85
2-Methylbutane*	NACA	99.4	92.5	81.1	36.6	1.20	1.13	2.89
2,2-Dimethylbutane*	NACA	98	90.0	79.2	35.7	1.17	1.12	2.43
2,3-Dimethylbutane*	NACA	----	91.7	80.5	36.3	1.19	1.13	2.45
2,2,3-Trimethylbutane*	NACA	----	90.5	79.6	35.9	1.18	1.15	2.15
2-Methylpentane*	NACA	99.3	93.0	81.5	36.8	1.21	1.14	2.46
3-Methylpentane*	NACA	98	92.7	81.3	36.7	1.20	1.15	2.48
2,3-Dimethylpentane*	NACA	----	92.2	80.9	36.5	1.20	1.18	2.22
2,4-Dimethylpentane*	P	99	89.9	79.2	35.7	1.17	1.16	2.17
Ethene*	O ⁶	99.5	184.5	151.4	68.3	2.24	1.14	7.40
Propene*	P	99	113.4	97.1	43.8	1.44	1.13	5.04
1-Butene*	P	99	111.5	95.7	43.2	1.42	1.15	3.87
1-Pentene*	NACA	----	110.0	94.5	42.6	1.40	1.13	3.07
1-Hexene*	NACA	----	108.5	93.4	42.1	1.38	1.17	2.67
2-Methyl-1-propene*	P	----	95.0	83.1	37.5	1.23	1.13	3.83
2-Methyl-1-butene*	NACA	----	99.5	86.5	39.0	1.28	1.15	3.12
3-Methyl-1-butene*	NACA	----	106.9	92.1	41.5	1.36	1.14	3.11
2-Ethyl-1-butene*	NACA	----	100.3	87.1	39.3	1.29	1.16	2.65
2-Methyl-1-pentene*	NACA	----	101.2	87.8	39.6	1.30	1.23	2.80
4-Methyl-1-pentene	NACA	----	104.0	89.9	40.5	1.33	1.15	2.62

1,3-Butadiene	NBS ⁷	99.9	144.4	120.9	54.5	1.79	1.18	4.34
1,2-Butadiene	NBS	99.9	154.3	128.5	58.0	1.90	1.16	4.27
cis 1,3-Pentadiene	NBS	99.9	121.0	103.0	46.5	1.53	1.19	3.47
trans 1,3-Pentadiene	NBS	99.9	118.5	101.1	45.6	1.50	1.16	3.37
1,4-Pentadiene	NBS	99.9	121.5	103.4	46.6	1.53	1.14	3.33
2,3-Pentadiene	NBS	99.8	133.2	112.3	50.7	1.66	1.18	3.43
1,2-Pentadiene	NBS	99.5	136.4	114.8	51.8	1.70	1.19	3.45
1,5-Hexadiene	NBS	99.8	114.5	98.0	44.2	1.45	1.17	2.83
2-Methyl-1,3-butadiene	NBS	99.5	116.7	99.7	45.0	1.48	1.17	3.41
2,3-Dimethyl-1,3-butadiene	NBS	99.9	106.8	92.2	41.6	1.36	1.18	2.85
Propyne*	NACA	98	189.1	154.9	69.9	2.29	1.18	5.86
1-Butyne*	NACA	99.7	155.0	128.9	58.1	1.91	1.19	4.36
1-Pentyne*	NACA	----	140.0	117.4	52.9	1.74	1.21	3.51
1-Hexyne*	NACA	----	127.0	107.5	48.5	1.59	1.23	2.97
4-Methyl-1-pentyne*	NACA	----	116.9	99.8	45.0	1.48	1.19	2.87
2-Butyne*	NACA	----	135.8	114.1	51.5	1.69	1.19	4.36
3-Hexyne*	NACA	----	118.0	100.6	45.4	1.49	1.26	3.05
Cyclohexane*	----	----	98.4	85.7	38.7	1.27	1.16	2.65
Benzene	----	----	104.5	90.3	40.7	1.34	1.23	3.34

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*Data from reference 1.

¹U_g calculated from equation (2).²g calculated from equation (1) using A_t = 5.07 sq cm and A_p = 11.25 sq cm (reference 1).³The Matheson Company, Inc.⁴Phillips Petroleum Company.⁵Prepared jointly by National Bureau of Standards and NACA.⁶Ohio State University Research Foundation, A.P.I. Research Project 45.⁷Standard samples prepared by National Bureau of Standards.

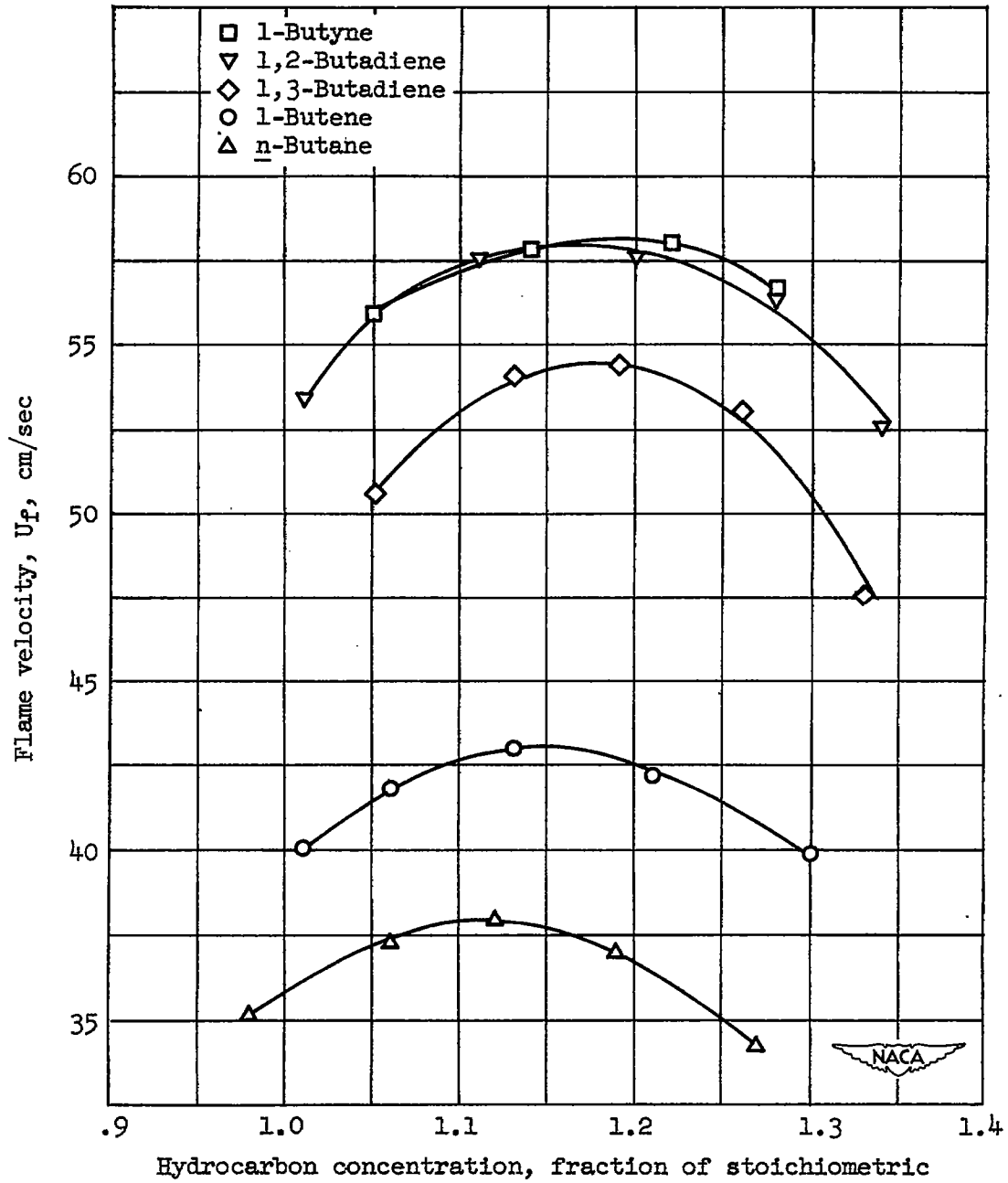


Figure 1. - Fundamental flame velocity of hydrocarbons with 4 carbon atoms in the straight chain.

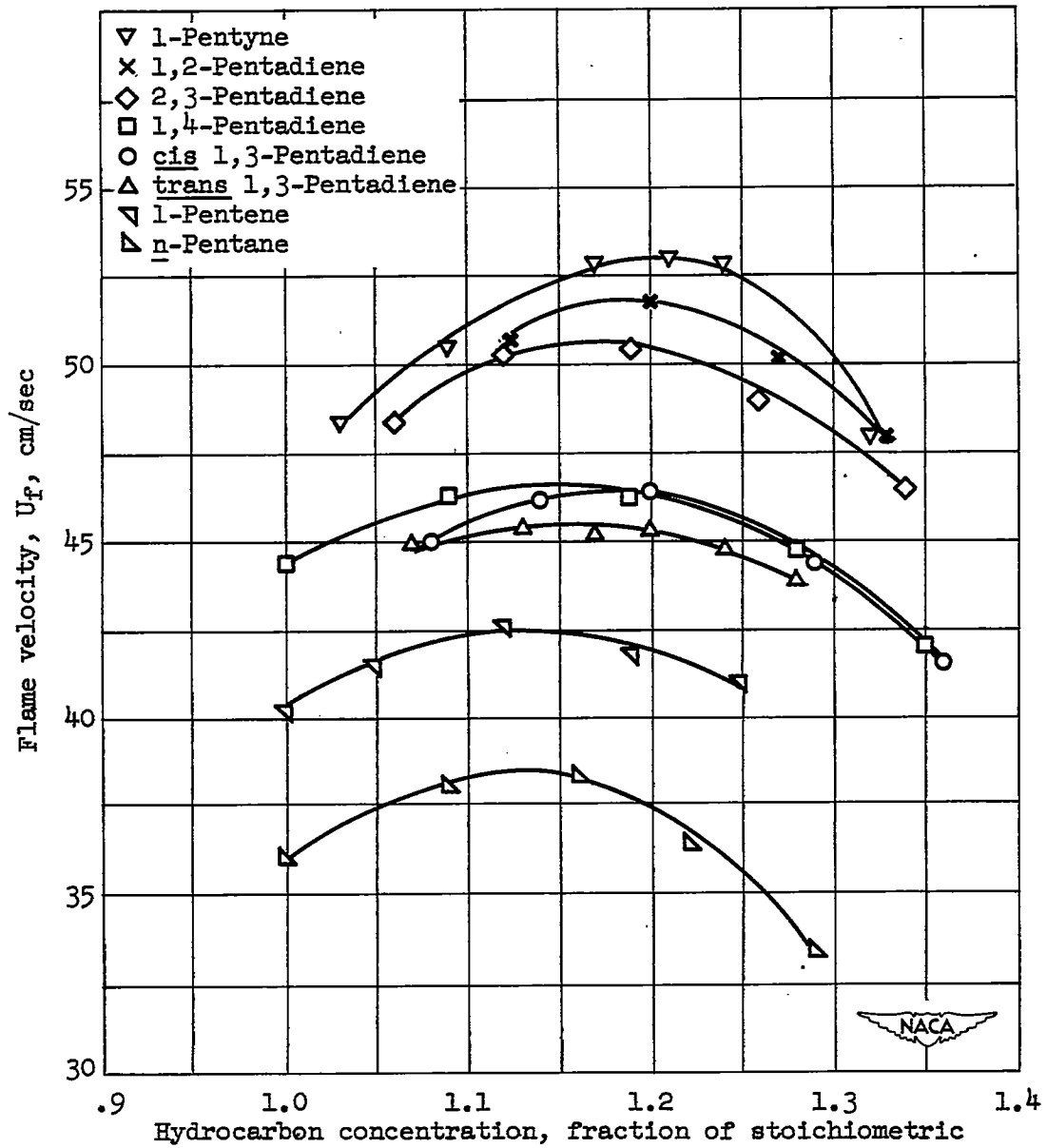


Figure 2. - Fundamental flame velocity of hydrocarbons with 5 carbon atoms in the straight chain.

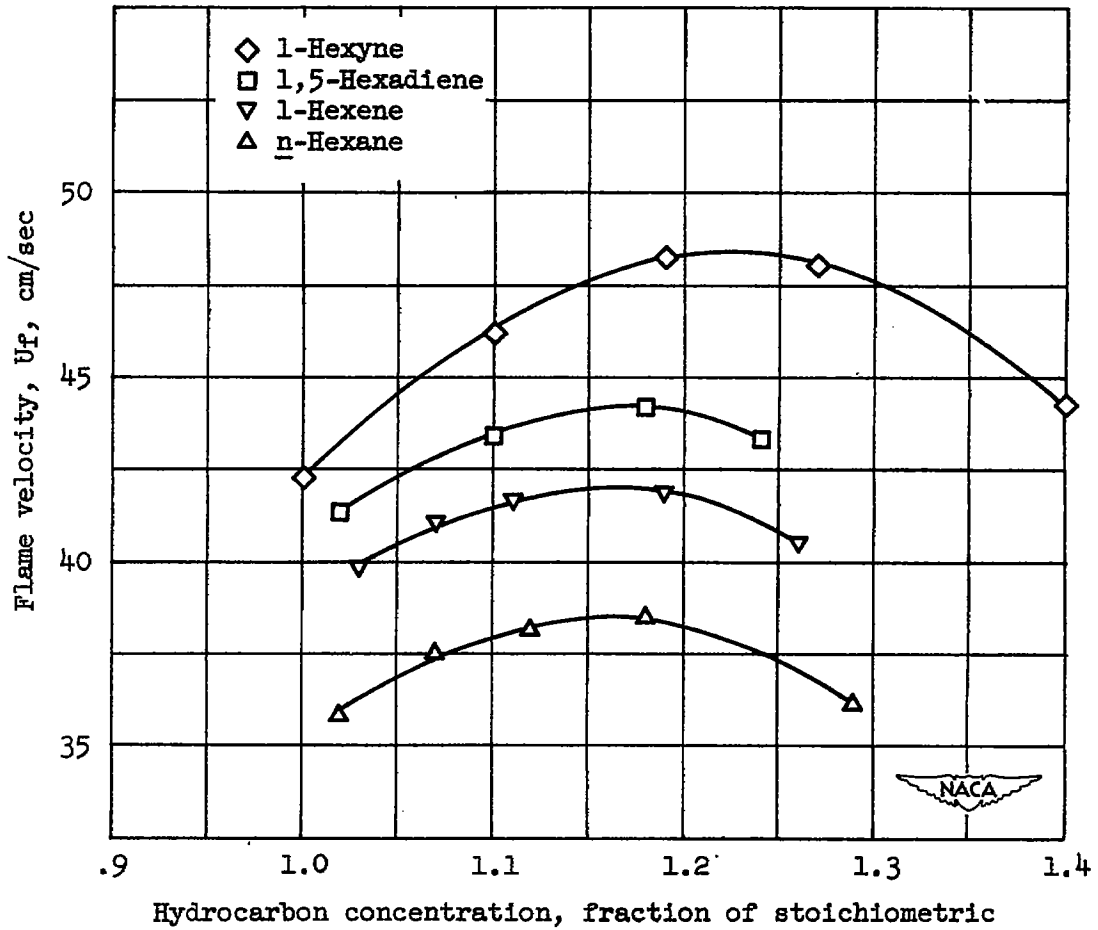


Figure 3. - Fundamental flame velocity of hydrocarbons with 6 carbon atoms in the straight chain.

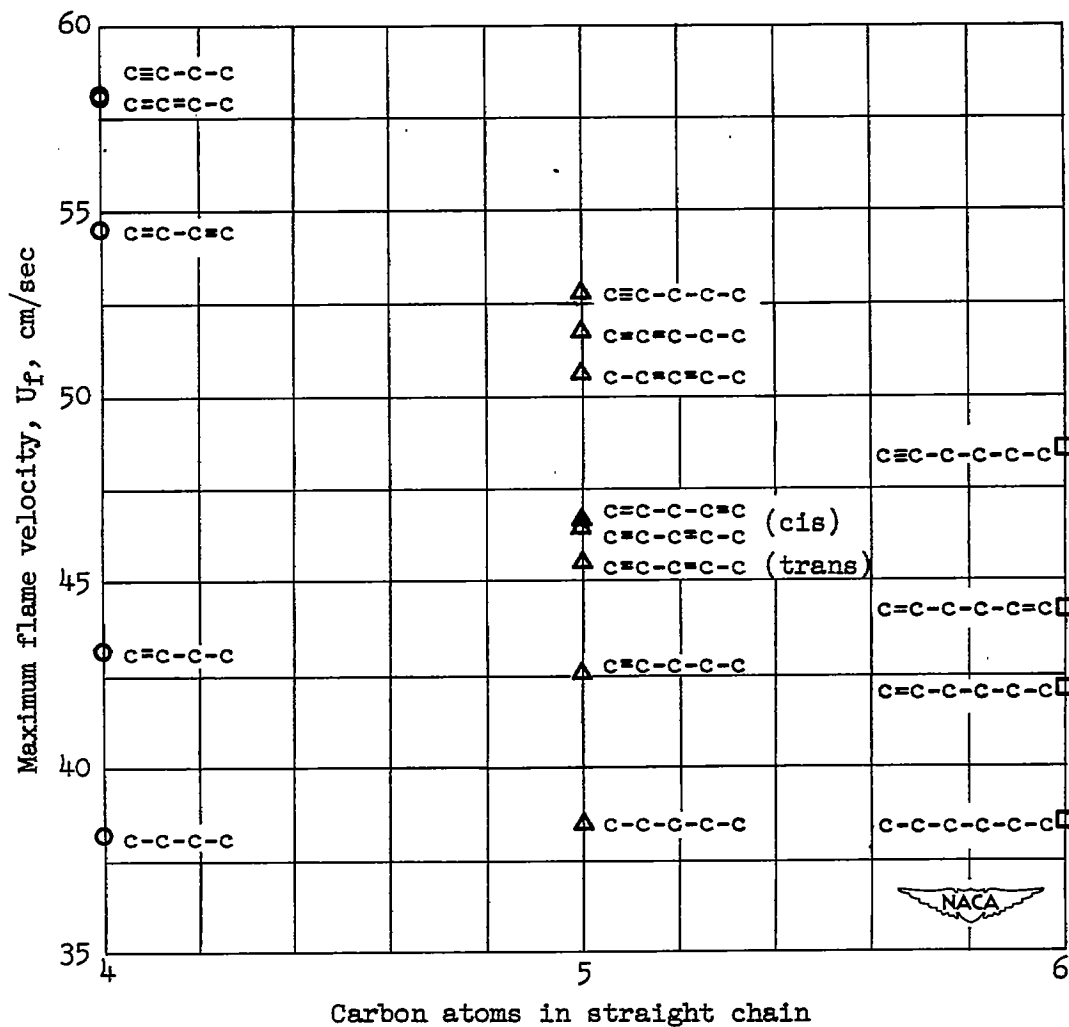


Figure 4. - Maximum fundamental flame velocities of normal aliphatic hydrocarbons.

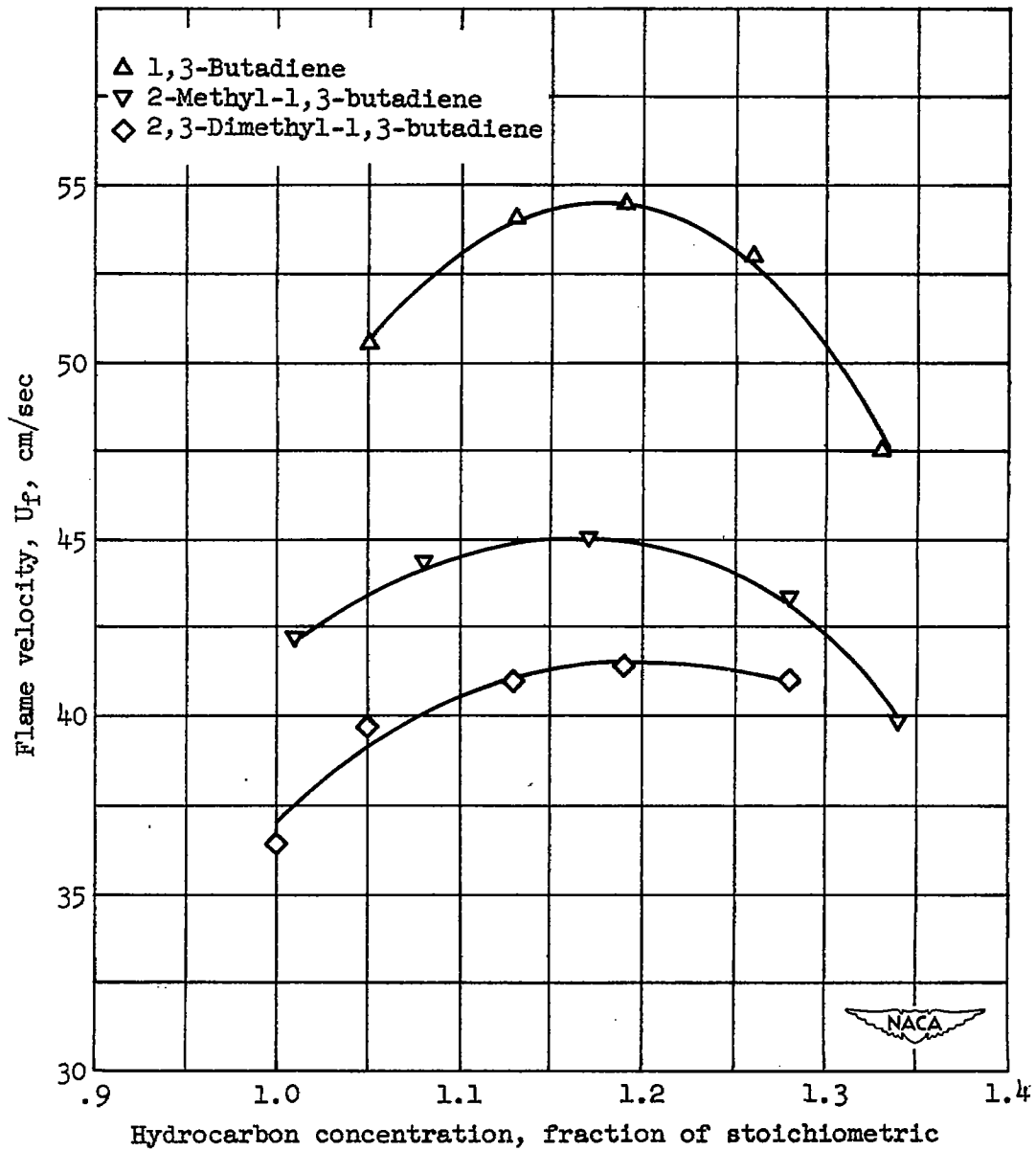


Figure 5. - Effect of methyl substitution on fundamental flame velocity.

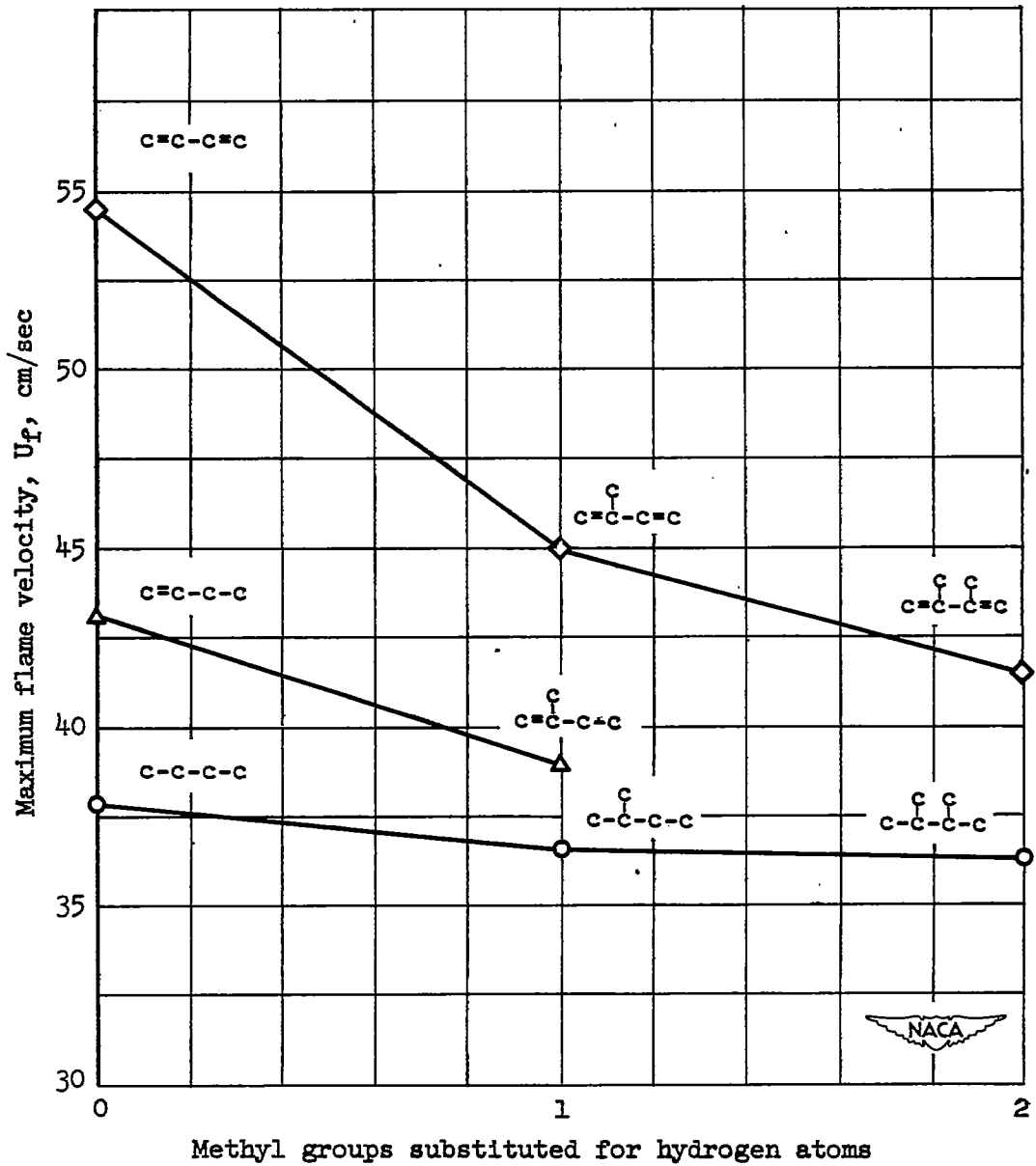


Figure 6. - Effect of methyl substitution on maximum fundamental flame velocity.