of results on the reference fuel and fuel H containing additives A and C, similar ash-type materials, and additive B, a nonash compound. In the reference fuel, additive A was effective to 300° F., while additive B was effective even at 350° F. fuel outlet temperature. The amount of additive in fuel H required to produce negligible pressure drop after 2.5 hours was remarkably low—on the order of 0.01 volume %.

Recirculation of the fuel in this test apparently results in additive depletion, as shown in Figure 11, where the standard test is compared to a one-pass test for a JP-4 type fuel containing additive C. In actual practice where once-through operation is used, the additive might be expected to perform considerably better than indicated in the recirculation type test.

SUMMARY

The tendency of certain aircraft turbine fuels to form insoluble material during passage through a heat exchanger has been evaluated in a laboratory bench test. A major factor in deposition appears to be the temperature; an increase in temperature may either increase or decrease deposition, depending on fuel characteristics. The particles formed are approximately 0.1 to 1.0 micron in diameter before flocculation and closely resemble ordinary distillate fuel oil sludges in appearance and composition. Simple treatments have only a small effect on the formation of insolubles, but sludge dispersants of the type marketed for distillate furnace oils are effective in the laboratory bench test.

This test is, in effect, a miniature of the prototype system. The results obtained so far are encouraging. Certain changes are being considered in order to more nearly functionally duplicate the prototype. Other investigators are evaluating the use of bomb-type tests, followed by filtration. Although such tests subject the fuel to a different time-temperature relationship they may be useful and are of interest because of their simplicity.

Stability characteristics will continue to be a factor limiting the storage and use of aircraft turbine fuels and, therefore, deserve continued study.

LITERATURE CITED

(1) Altman, R. W., U. S. Air Corps, Tech. Rept. **5636**, Sept. 25, 1947.
(2) ASTM Standards on Petroleum Products and Lubricants, Appendix 4, 1952.
(3) Bender, R. O., Lawson, N. D., and Kernen, A. R., presented at Regional Technical Meeting, Western Petroleum Refiners Assoc., Beaumont, Tex., Feb. 7–8, 1952.
(4) Finn, R. F., and Lifson, W. E., Esso Laboratories, "Factors Affecting Water Content of Aviation Fuels," Sept. 21, 1953.
(5) *Lubrication*, **34**, 43 (1948).
(6) Murray, H. A., *Oil Gas J.*, **50**, 218 (March 29, 1952).
(7) Nixon, A. C., Cole, C. A., and Walters, E. L., presented before the Division of Petroleum Chemistry at the 125th Meeting, ACS, Kansas City, March 1954.
(8) Schwartz, F. G., Ward, C. C., and Smith, H. M., presented at the Natl. Diesel Engine Meeting, SAE, Nov. 3–4, 1953.
(9) Shell Development Co., Emeryville, Calif., unpublished data.
(10) Thompson, R. B., Durge, L. W., and associates, Ind. Eng. Chem., **43**, 935 (1951).
(11) Thompson, R. B., Durge, L. W., and Chenicek, J. A., *Ibid.*, **41**, 2715 (1949).
(12) Walker, D. C., and Conway, H. S., *Anal. Chem.*, **25**, 923 (1953).
(13) Walters, E. L., Minor, H. B., and Yabroff, D. L., Ind. Eng. Chem., **41**, 1723(1949).
(14) Walters, E. L., Yabroff, D. L., and Minor, H. B., *Ibid.*, **40**, 423 (1948).
(15) Yabroff, D. L., and Walters, E. L., Ind. Eng. Chem., **32**, 83 (1940).
(16) Yule, H. A., and Wilson, C. P., Jr., *Ibid.*, **23**, 1254 (1931).

Received for review March 4, 1954. Accepted June 11, 1954.

END OF SYMPOSIUM

Reprints of this symposium may be purchased for 75 cents each from the Reprint Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington 6, D. C.

Minimum Spontaneous Ignition Temperatures of Combustibles in Air

M. G. ZABETAKIS, A. L. FURNO, AND G. W. JONES
Explosives and Physical Sciences Division, U. S. Bureau of Mines, Pittsburgh, Pa.

IN DETERMINING the relative hazards associated with various vapor-air mixtures in contact with a specific surface at a particular temperature and pressure, the Bureau of Mines has in the past employed the standard ASTM autogenous ignition temperature apparatus (ASTM Designation D 286–30) as well as a modification of this apparatus (*9*). Since only one electric heater was used in this modified apparatus, there was a temperature differential along the axis of the test flask. Moreover, because of the large amount of metal used in the construction of this apparatus, 1 or more hours often were required to change the temperature between successive tests. Accordingly, a new ignition temperature apparatus (I-8) has been developed which makes the determination of minimum spontaneous ignition temperatures—autogenous ignition temperatures—more rapid, accurate, and economical.

APPARATUS

The I-8 apparatus (Figure 1) consists, as before, of a commercial 1200-watt electric crucible furnace with a vertical cylindrical well 5 inches in diameter and 5 inches in depth. The addition of two auxiliary heaters to this standard furnace has eliminated the temperature gradient noted in the previous apparatus (*9*).

A 200-cc. borosilicate glass Erlenmeyer flask, *a*, is placed in the crucible well (other materials have been used to determine the effect of the surface on the ignition temperature). The temperature of the neck, midsection, and base of the flask are determined by means of the three iron-constantan thermocouples, *b*, *c*, and *d*. These temperatures are recorded continuously and sequentially by a 12-point electronic temperature recorder (Figure 2). When thermal equilibrium has been attained, the temperature along the axis of the flask is within 1° C. of the temperature recorded by the recorder (the temperature of the neck,

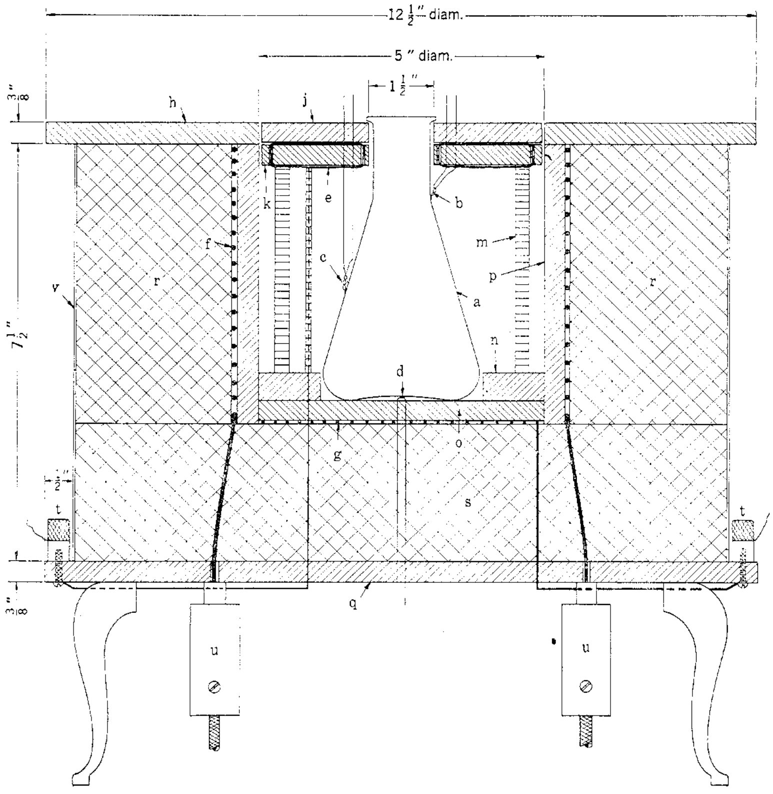

Figure 1. I-8 Ignition Temperature Apparatus

midsection, and base of the Erlenmeyer flask are kept within 0.5° C. of each other during a test). The current through each of the three heaters, *e*, *f*, and *g*, is controlled individually by one of three variable autotransformers. Disks *h*, *j*, *k*, *n*, *o*, and *q* are made of transite; *h* and *q* are part of the original furnace, *j* is a cover plate, *k* and *o* are used as forms for the neck and base heaters, respectively, and *n* holds the ceramic rods *m* which support *k* and *j*. Alundum core *p*, insulation *r* and *s*, retaining cylinder *v*, and electrodes *u* are part of the original furnace. Binding posts *t* were added for use with the auxiliary heaters.

PROCEDURE

A test with the I-8 apparatus involves three steps—temperature control, introduction of sample, and observation. The temperature of the air in the test flask is controlled by adjusting the current flow in the three heaters. While the flask temperature is being adjusted to the desired temperature, the flask is kept covered and the temperatures of the three thermocouples in the furnace are recorded continuously. When the temperature has been established, a sample of the combustible liquid to be tested is introduced into the flask by means of a 0.25- or 1.0-ml. hypodermic syringe equipped with a 3-inch No. 19 stainless steel needle. Gases which are to be tested are first liquefied (*9*); the combustible solids that have been tested were introduced into the flask in the solid state or suspended in the flask from an insulating support. In an actual test, the room is first darkened, the sample is introduced into the test flask (Figure 2), and at the same time an electric timer is started. The electric timer is stopped at the instant of ignition (as evidenced by the appearance of a flame). If no ignition occurs after 5 minutes (or longer, if a plot of the spontaneous ignition temperature against time lag before ignition warrants a longer observation period) the test is discontinued, and the test flask is swept out with dried, filtered air, in preparation for the next run. Once the minimum ignition temperature has been determined with a given quantity of sample, the sample volume is changed. In this way the tests are repeated until a number of volumes have been tried. It is found that samples with a volume larger or smaller (depending on the combustible tested) than one particular volume—the critical volume—yield higher minimum ignition temperatures than the sample with the "critical" volume. It is important to vary the volume of the samples until this critical volume is determined. As the tests are made, the ignition temperature is plotted against the time lag before ignition for the various volumes of sample. As the minimum spontaneous ignition temperature is approached the time lag increases appreciably for a small change in ignition temperature. Typical ignition temperature–time lag graphs are given in Figure 3 for *n*-heptane and *n*-decane. Similar graphs have been published for eight members of the aromatic series (*11*) and several fuel blends (*3*).

IGNITION TEMPERATURE

Tests at Atmospheric Pressure. The minimum ignition temperatures and the corresponding time lags determined with the I-8 apparatus for a number of combustibles in air at 1 atmosphere pressure are given in Table I. A limited number of experiments were conducted in oxygen with the same apparatus, but are not included in the table.

Spontaneous ignition temperature experiments are basically oxidation experiments. Earlier research on the oxidation of hydrocarbons (*6*, *10*) has indicated that two basically different mechanisms can take part in the oxidation of paraffin hydrocarbons. The first is a low temperature mechanism that involves an initial formation of peroxides and a subsequent splitting of the molecule into several radicals, including one or more alkyl radi-

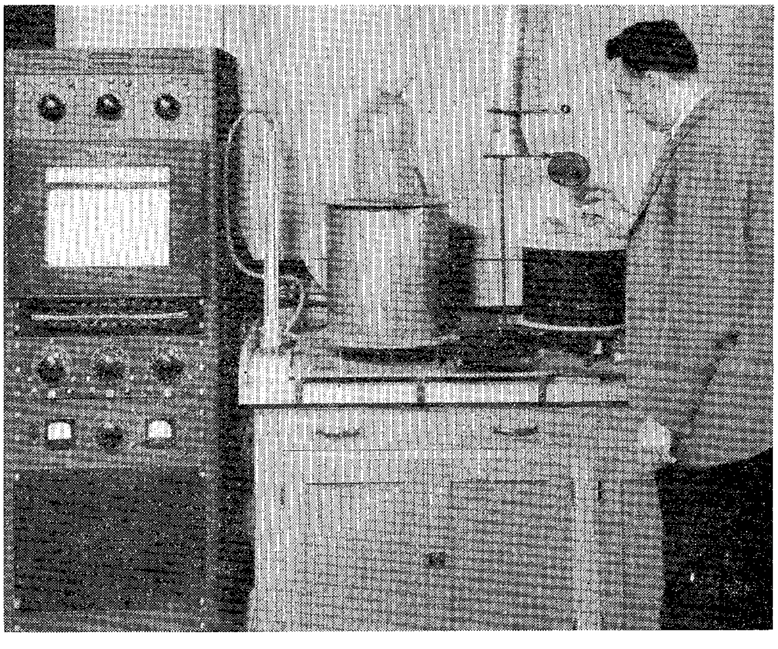

Figure 2. Ignition Temperature Apparatus, Electric Timer, Temperature Control Panel, and Electronic Recorder

Table I. Minimum Spontaneous Ignition Temperatures and Time Lags before Ignition of Combustibles in Air

(1 atmosphere pressure, I-8 apparatus)

Combustible	Formula	Min. Spontaneous Ignition Temp. ° C.	Min. Spontaneous Ignition Temp. ° F.	Time Lag, Sec.
Acetanilide	C_8H_9NO	547	1017	12
Acetophenone	C_8H_8O	571	1060	13
Acetylacetone	$C_5H_8O_2$	340	644	43
Acetyl chloride	C_2H_3OCl	390	734	5
Adipic acid	$C_6H_{10}O_4$	422	792	19
Aircraft hydraulic fluid, AN-O-366	...	225	437	141
Aldol	$C_4H_8O_2$	248	478	26
n-Amyl alcohol	$C_5H_{12}O$	300	572	13
tert-Amyl alcohol	$C_5H_{12}O$	437	819	9
n-Amyl ether	$C_{10}H_{22}O$	171	340	18
Amyl nitrite, USP XII	$C_5H_{11}NO_2$	209	408	12
n-Amyl propionate	$C_8H_{16}O_2$	378	712	2
Aniline	C_6H_7N	617	1143	4
Anthracene	$C_{14}H_{10}$	540	1004	17
Aviation gasoline, Grade 100/130	...	440	824	3
Grade 115/145	...	471	880	5
Aviation jet fuel, Grade JP-1	...	228	442	120
Grade JP-3	...	238	460	187
Grade JP-4	...	242	468	185
Benzene	C_6H_6	562	1044	32
Benzyl benzoate	$C_{14}H_{12}O_2$	481	898	21
Benzyl chloride	C_7H_7Cl	585	1085	17
Biphenyl	$C_{12}H_{10}$	566	1051	39
2-Biphenylamine	$C_{12}H_{11}N$	452	846	9
Bromobenzene	C_6H_5Br	566	1051	9
n-Butane	C_4H_{10}	405	761	6
sec-Butyl alcohol	$C_4H_{10}O$	406	763	24
n-Butylbenzene	$C_{10}H_{14}$	412	774	9
sec-Butylbenzene	$C_{10}H_{14}$	418	784	21
tert-Butylbenzene	$C_{10}H_{14}$	450	842	80
n-Butyl bromide	C_4H_9Br	265	509	10
n-Butyl stearate	$C_{22}H_{44}O_2$	355	671	2
n-Butyric acid	$C_4H_8O_2$	452	846	19
Chlorobenzene	C_6H_5Cl	638	1180	9
Cumene	C_9H_{12}	424	795	31
Cyclohexane	C_6H_{12}	260	500	206
Cyclohexanol	$C_6H_{12}O$	300	572	40
Cyclohexanone	$C_6H_{10}O$	420	788	17
Cyclohexyl acetate	$C_8H_{14}O_2$	334	633	10
p-Cymene	$C_{10}H_{14}$	436	817	22
n-Decane	$C_{10}H_{22}$	208	406	124
1,4-Diethylbenzene	$C_{10}H_{14}$	430	806	10
Diethyl ketone	$C_5H_{10}O$	452	846	8
3,3-Diethylpentane	C_9H_{20}	290	554	4
Diphenylamine	$C_{12}H_{11}N$	634	1173	60
Diphenyl ether	$C_{12}H_{10}O$	618	1144	15
Diphenylmethane	$C_{13}H_{12}$	486	907	28
n-Dodecane	$C_{12}H_{26}$	204	399	214
Dry-cleaning solvent, 140° F.	...	233	451	182
Ethane	C_2H_6	515	959	10
Ethylbenzene	C_8H_{10}	432	810	18
Ethylcyclobutane	C_6H_{12}	212	414	33
Ethylcyclohexane	C_8H_{16}	262	504	35
Ethylcyclopentane	C_7H_{14}	262	504	57
Ethyl formate	$C_3H_6O_2$	455	851	14
Formaldehyde (35.5% by wt.)	...	424	795	14
n-Heptane	C_7H_{16}	223	433	101
n-Heptane plus iso-octane	75–25	237	459	76
	60–40	248	478	55
	50–50	268	514	18
	40–60	283	541	10
	35–65	319	606	5
	30–70	334	633	5
	25–75	367	693	4
	15–85	387	729	5
n-Hexane	C_6H_{14}	234	453	57
n-Hexadecane	$C_{16}H_{34}$	205	401	141
n-Hexadecane plus 1-methylnaphthalene	75–25	357	675	5
	50–50	370	698	3
n-Hexyl ether	$C_{12}H_{26}O$	187	369	37
Isoamyl alcohol	$C_5H_{12}O$	347	657	13
Isobutyl acetate	$C_6H_{12}O_2$	423	793	4
Isobutylamine	$C_4H_{11}N$	378	712	4
Isobutylbenzene	$C_{10}H_{14}$	428	802	16
Isobutylene	C_4H_8	465	869	91
Iso-octane	C_8H_{18}	418	784	27
Kerosine	...	229	444	210
Methylal	$C_3H_8O_2$	237	459	18
o-Methylcyclohexanol	$C_7H_{14}O$	296	565	40
p-Methylcyclohexanol	$C_7H_{14}O$	295	563	40
1-Methylnaphthalene	$C_{11}H_8$	529	984	23
Naphthalene (78° crude)	$C_{10}H_8$ (crude)	526	979	18
n-Nonane	C_9H_{20}	206	403	130
n-Octane	C_8H_{18}	220	428	132
n-Pentane	C_5H_{12}	287	549	10
Petroleum ether	...	288	550	15
Stoddard solvent	...	229	444	123
n-Tetradecane	$C_{14}H_{30}$	202	396	158
2,2,3,3-Tetramethylpentane	C_9H_{20}	430	806	77
2,2,4-Trimethylpentane	C_8H_{18}	418	784	27
Toluene	C_7H_8	536	997	72
m-Xylene	C_8H_{10}	528	982	61
o-Xylene	C_8H_{10}	464	867	36
p-Xylene	C_8H_{10}	529	984	69

cals. In low temperature oxidation the initial attack appears to be on a C—H bond not associated with a —CH_3 group. Accordingly, the alkyl radical which splits off of the oxidized molecule contains one or more —CH_3 groups. This mechanism is reflected in the relative minimum spontaneous ignition temperatures of various paraffin hydrocarbons that depend more on the number and positions of the —CH_3 groups than on the total number of carbon atoms in the molecule. A correlation parameter involving the total number of carbon atoms as well as the number of —CH_3 groups and their position in the paraffin hydrocarbon molecule—a parameter termed the average carbon chain length—leads to a number of interesting correlations. The second mechanism is a high temperature mechanism. It differs from the first in that it involves little if any peroxide formation (*6*). However, in the present paper the same correlation parameter has been applied to both the high and low temperature regions.

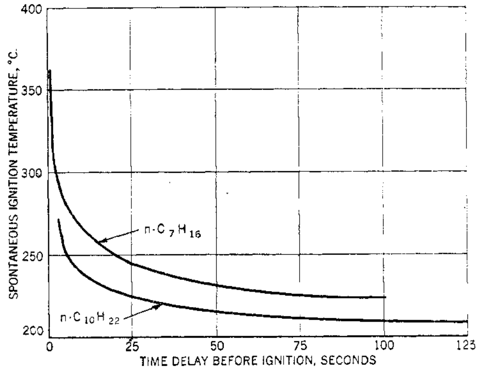

Figure 3. Spontaneous Ignition Temperature and Corresponding Time Lag before Ignition in Air at 1 Atmosphere

If a paraffin hydrocarbon that contains a number, M, of —CH_3 groups is considered, the total number of straight carbon chains with a —CH_3 on both ends that could be formed from this paraffin hydrocarbon is

$$\sum_{n=1}^{M} (M - n) = M\left(\frac{M-1}{2}\right)$$

Since there may be g_i chains, each containing N_i carbon atoms,

$$\sum_i g_i = M\left(\frac{M-1}{2}\right)$$

The average chain length, $L_{\text{av.}}$ (weighting equally all possible straight-chain lengths), is

$$L_{\text{av.}} = \frac{\sum_i g_iN_i}{\sum_i g_i} = \frac{\sum_i g_iN_i}{M\left(\frac{M-1}{2}\right)} = \frac{2\sum_i g_iN_i}{M(M-1)}$$

Thus, *n*-nonane and 2,2,3,3-tetramethylpentane each have nine carbon atoms, but their average carbon chain lengths, calculated as above, are not the same. For these two paraffin hydrocarbons

Combustible	M	i	N_i	g_i	$L_{\text{av.}}$
n-Nonane	2	1	9	1	9.0
2,2,3,3-Tetramethylpentane	6	1	3	4	3.9
		2	4	8	
		3	5	3	

These data are included in Table II and a graph of $L_{\text{av.}}$ against the corresponding minimum spontaneous ignition temperature

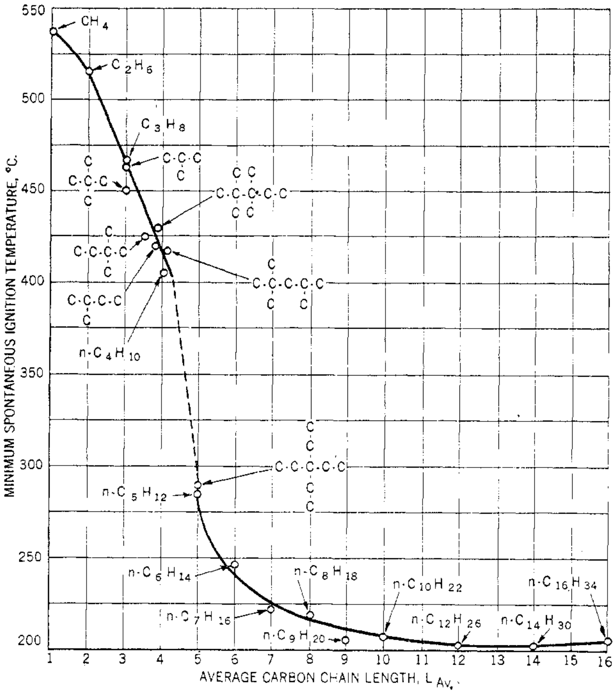

Figure 4. Minimum Spontaneous Ignition Temperatures of Paraffin Hydrocarbons in Air as Function of Average Carbon Chain Length

is given in Figure 4. The minimum spontaneous ignition temperatures in Figure 4 fall into two general regions—those below 290° C. (above $L_{av.} \approx 5$) and those above 405° C. (below $L_{av.} \approx 4$). The former are characterized by a long main chain and long side chains, and the latter by short main and side chains or a long main chain and many short side chains. For example, 3,3-diethylpentane and 2,2,3,3-tetramethylpentane each contain a total of nine carbon atoms and have a main chain of five carbon atoms. However, the former compound has two ethyl side chains compared to four methyl side chains in the latter structure so that the ignition temperature of 3,3-diethylpentane is 140° C. lower and its average chain length 1.1 C's greater than the corresponding values for 2,2,3,3-tetramethylpentane. These two ignition temperature regions apparently coincide with those discussed by Mulcahy (*6*) and Frank, Blackham, and Swarts (*1*).

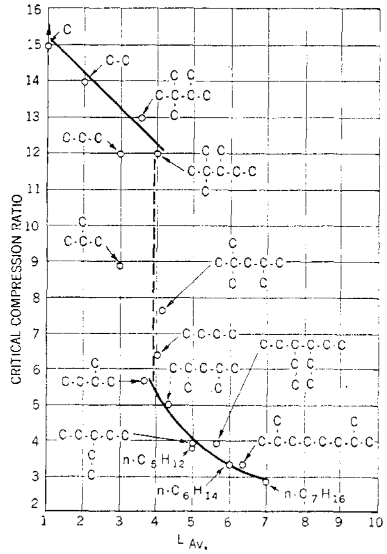

Figure 5. Critical Compression Ratios of Paraffin Hydrocarbons as Function of Average Carbon Chain Length

Table II. Minimum Spontaneous Ignition Temperatures of Paraffin Hydrocarbons in Air

(1 atmosphere pressure)

Combustible	Av. Carbon Chain Length ($L_{av.}$)	Min. Spontaneous Ignition Temp., ° C.	Reference
Methane	1	537	(*8*)
Ethane	2	515	Table I
Propane	3	466	(*8*)
Isobutane	3	462	(*9*)
Neopentane	3	450	(*8*)
2,2-Dimethylbutane	3.5	425	(*8*)
Isopentane	3.7	420	(*9*)
2,2,3,3-Tetramethylpentane	3.9	430	Table I
n-Butane	4.0	405	Table I
2,2,4-Trimethylpentane	4.2	418	Table I
n-Pentane	5.0	287	Table I
3,3-Diethylpentane	5.0	290	Table I
n-Hexane	6.0	248	Table I
n-Heptane	7.0	223	Table I
n-Octane	8.0	220	Table I
n-Nonane	9.0	206	Table I
n-Decane	10.0	208	Table I
n-Dodecane	12.0	204	Table I
n-Tetradecane	14.0	202	Table I
n-Hexadecane	16.0	205	Table I

Another interesting curve is obtained by plotting $L_{av.}$ against the critical compression ratio for various paraffin hydrocarbons. This has been done in Figure 5, using the data of Lovell, Campbell, and Boyd (*5*) (Table III). Like the minimum spontaneous ignition temperatures, the critical compression ratio values appear to fall into one of two regions, separated in this case by $L_{av.} \approx 4$.

A considerable amount of work has been done in the past on the spontaneous ignition temperatures of liquid mixtures. Because of their industrial importance, mixtures of *n*-heptane and 2,2,4-trimethylpentane were investigated (Table I). The low and high ignition temperature regions are again evident (Figure 6). If time lags before ignition of these mixtures and of the paraffin hydrocarbons listed in Tables I and IV are plotted against their corresponding minimum spontaneous ignition temperatures, the graph (Figure 7) again may be divided into two regions. To approximately 330° C., time lags before ignition decrease as the minimum spontaneous ignition temperatures increase; above approximately 370° C., the time lags increase with increasing temperature. For the hydrocarbon investigated, a decrease in pressure appears both to increase the minimum spontaneous ignition temperatures and to decrease the corresponding time lags before ignition (Figure 7) indicating that, at least for the three paraffin hydrocarbons investigated, the oxidation mechanism changes in going from 1 atmosphere to 0.5 atmosphere.

Tests at Low Pressures. The I-8 apparatus has been used also to determine the minimum spontaneous ignition tempera-

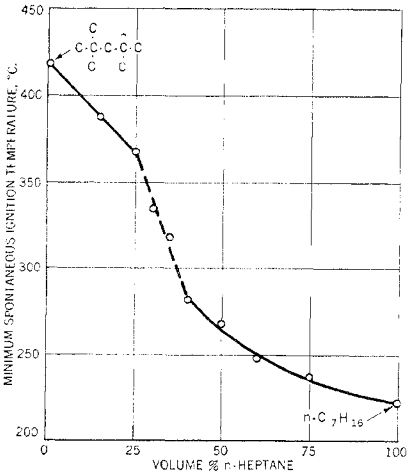

Figure 6. Minimum Spontaneous Ignition Temperatures of Iso-octane–*n*-Heptane Mixtures in Air at 1 Atmosphere Pressure

tures at reduced pressures. For these determinations, the apparatus is housed in a stainless steel shell which is evacuated to the desired pressure. A bell jar forms the top of the apparatus (Figure 2). A capillary tube used for the introduction of the liquid sample passes through the bell jar and into the 200-cc. Erlenmeyer flask. This tube is sealed except at the instant the sample is introduced with a hypodermic syringe. Data obtained with this apparatus at 0.5 atmosphere pressure are given in Table IV. Minimum spontaneous ignition temperature data also were obtained for JP-4 grade jet fuel in air at 230 and 180 mm. of mercury absolute pressure. A graph of the low pressure minimum spontaneous ignition temperature data for this jet fuel in air is given in Figure 8. As with the other combustibles listed in Table IV, the minimum spontaneous ignition temperature of this fuel increases as the pressure decreases.

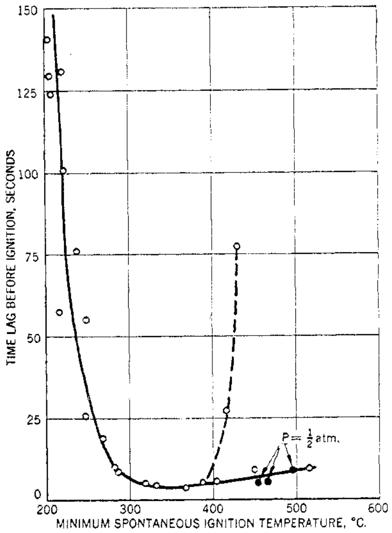

Figure 7. Minimum Spontaneous Ignition Temperature and Corresponding Time Lag before Ignition in Air at 1 Atmosphere

Paraffin hydrocarbons of Tables I and IV

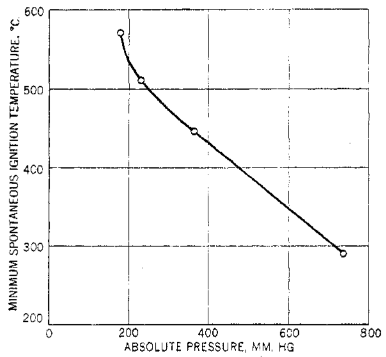

Figure 8. Effect of Pressure on Minimum Spontaneous Ignition Temperature of Aviation Jet Fuel Grade JP-4 in Air

Table III. Critical Compression Ratios of Paraffin Hydrocarbons (*5*)

Combustible	Av. Carbon Chain Length ($L_{av.}$)	Critical Compression Ratio
Methane	1.0	>15
Ethane	2.0	14.0
Propane	3.0	12.0
Isobutane	3.0	8.9
Isopentane	3.7	5.7
2,3,3-Trimethylbutane	3.6	13.0
n-Butane	4.0	6.4
2,2,3-Trimethylpentane	4.0	12.0
2,2,4-Trimethylpentane	4.2	7.7
2,4-Dimethylpentane	4.3	5.0
n-Pentane	5.0	3.8
3-Ethylpentane	5.0	3.9
3,4-Diethylhexane	5.7	3.9
n-Hexane	6.0	3.3
2,7-Dimethyloctane	6.3	3.3
n-Heptane	7.0	2.8

Table IV. Minimum Spontaneous Ignition Temperatures of Combustibles in Air

Combustible	Min. Spontaneous Ignition Temp.			
	370 mm. Hg		742 ± 8 mm. Hg	
	° C.	° F.	° C.	° F.
Aviation jet fuel, Grade JP-4	444	831	242	468
Aircraft hydraulic fluid, Grade AN-0-366	448	838	225	437
Aviation jet fuel, Grade JP-3	449	840	238	460
n-Decane	458	856	208	406
Aviation jet fuel, Grade JP-1	462	864	228	442
n-Octane	465	869	220	428
n-Hexane	497	927	234	453
Aviation gasoline, Grade 100/130	553	1027	440	824
Aviation gasoline, Grade 115/145	573	1063	573	880

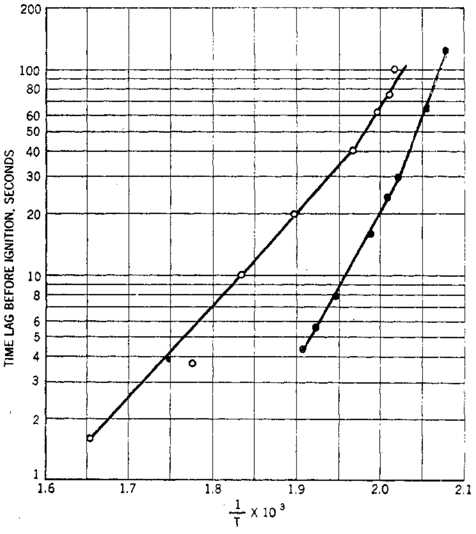

Figure 9. Time Lags before Ignition as Function of 1/T for Hydrocarbons in Air at 1 Atmosphere

○ ***n*-Heptane**
● ***n*-Decane**

ACTIVATION ENERGY

In the past, spontaneous ignition temperatures have been determined by at least eight different methods (*4*). Variables encountered include pressure, flow conditions, and various surface effects. As the flow conditions or apparatus were not comparable and the experimental pressures at which the experiments were conducted often differed appreciably, the minimum spontaneous ignition temperatures determined by various workers for the same combustibles varied significantly. In conducting the present experiments an attempt has been made to obtain a set of minimum spontaneous ignition temperatures at 1 atmosphere pressure that are not only consistent, but also suitable for use in the safety work which is one of the primary functions of the U. S. Bureau of Mines. The choice of a 200-cc. borosilicate glass Erlenmeyer test flask for use in the modified ignition temperature apparatus was made following tests on a number of flasks of various sizes, shapes, and materials. It is believed that the data reported are the best values available at this time for use in safety work at 1 atmosphere pressure.

These data also may be used for other purposes. Thus, plots of the spontaneous ignition temperature against the time lag before ignition (Figure 3) may be used to determine the maximum time during which a combustible-air mixture at a specified pressure may be held safely at a particular temperature. Similar data have been obtained by Mullins for flowing hydrocarbon-air mixtures at elevated temperatures (*7*). These data also may be used to obtain approximate activation energies for the oxidation of the combustibles tested (*7*).

The statistical interpretation of the Arrhenius equation (*2*) indicates that the rate of a collisional reaction is proportional to $\exp(-E/RT)$ where E is the activation energy. As the rate of reaction is inversely proportional to the time of reaction, the time of reaction should be related to the energy of activation as follows (*7*):

$$\ln \tau = \text{constant} + \frac{E}{RT}$$

Accordingly, a plot of $\ln \tau$ against $\frac{1}{T}$ should give a straight line with a slope equal to E/R. The data used to plot Figure 3 have been replotted in Figure 9 to show the straight lines that result from this type of plot. These graphs indicate that the activation energy for heptane-air ignitions at 1 atmosphere pressure in a borosilicate glass container decreases from 31 kcal. per mole over the temperature range 222° to 233° C. to 18 kcal. per mole over the temperature range 233° to 333° C. Similarly, the activation energy for decane-air ignitions at 1 atmosphere pressure decreases from 47 kcal. per mole over the temperature range 209° to 223° C. to 34 kcal. per mole over the temperature range 223° to 251° C. These activation energy calculations do not take into account the time required to vaporize the fuel which is probably negligible for temperatures near the minimum spontaneous ignition temperature that involve long time lags; these are the temperatures that yield 31 and 47 kcal. per mole for *n*-heptane and *n*-decane, respectively, in these examples.

LITERATURE CITED

(1) Frank, C. E., Blackham, A. U., and Swarts, D. E., IND. ENG. CHEM., **45**, 1753–9 (1953).
(2) Hinshelwood, C. N., "Kinetics of Chemical Change," Oxford University Press, New York, 1940.
(3) Jones, G. W., Zabetakis, M. G., and associates, Wright Air Development Center, Tech. Rept. **52–35** (Armed Serv. Tech. Information Agency, Catalog No. **AD 5805**), 1952.
(4) Jost, W., "Explosion and Combustion Processes in Gases," McGraw-Hill, New York, 1946.
(5) Lovell, W. G., Campbell, J. M. and Boyd, T. A., IND. ENG. CHEM., **26**, 1105–8 (1934).
(6) Mulcahy, M. F. R., *Trans. Faraday Soc.*, **45**, 537–41 (1949).
(7) Mullins, B. P., *Fuel*, **32**, 211–52, 327–79, 451–91 (1953).
(8) National Fire Protection Assoc., 60 Batterymarch St., Boston, National Fire Codes, **1**, 1951.
(9) Scott, G. S., Jones, G. W., and Scott, F. E., *Anal. Chem.*, **20** (1948).
(10) Walsh, A. D., *Trans. Faraday Soc.*, **42**, 269–83 (1946); **43**, 297–313 (1947).
(11) Zabetakis, M. G., Scott, G. S., and Jones, G. W., U. S. Bur. Mines, Rept. Invest. **4824**, 1951.

RECEIVED for review April 14, 1954. ACCEPTED June 23, 1954.
This research was supported in part by the Air Research and Development Command under Contracts (33-038) 50-1293-E and AF 18(600)-151.

Measuring Burning Quality of Distillate Fuels

G. I. WORRALL
Research Department, Standard Oil Co. (Indiana), Whiting, Ind.

BURNING quality of a distillate fuel oil is judged by the amount of soot or coke deposits formed in oil burners used in the home. Home burners vary widely in tendency to form deposits, but all burners rate fuels in essentially the same order of quality. It is of interest to petroleum refiners, therefore, to be able to measure the burning quality of fuel oils in order to ensure customer satisfaction.

Several laboratory methods have been used for evaluating burning quality. Studies of burner deposits and of flue gas soot have been reported (*6*, *7*, *9*), and combustion indexes relating to burning quality have been proposed (*2*, *7*). However, all of the reported methods are based on oils differing widely in physical properties. Attempts to confirm the methods by application to closely related fuels have failed. A more sensitive burner test is needed that can differentiate between fuels of almost identical gravity and boiling point. Precise data on burner deposits might then offer a firm basis with which simpler measurements of fuel quality could be correlated.

Burners for evaluating distillate fuel oils should be comparable to the home burners for which the oils are intended. Most commercial burners are of two types—atomizing or vaporizing. Atomizing burners usually spray fuel from a nozzle, whereas vaporizing burners evaporate fuel from a pool of hot oil by heat of combustion. Atomizing burners form only a sooty deposit on the interior heat exchange surfaces; vaporizing burners form a greater amount of sooty deposits, and, in addition, a cokelike deposit on the vaporizing surface. For laboratory purposes the vaporizing burner is desirable because both types of deposits can be studied in one test of short duration.

The pot burner is the most common of the vaporizing type and has been used in previous burner studies (*1*, *3*, *9*). Briefly, the burner consists of a vertical combustion cylinder surrounded by a rectangular metal shield. The lower part of the cylinder houses a perforated pot where oil vapors and air are mixed. Figure 1 is a schematic diagram of a typical pot used in commercial burners. When the burner operates, oil vapors rise from the pool of oil on the pot bottom, meet air drawn through the holes in the side, and burn. The hot gases rise upward through the combustion chamber and out the stack. Sooty deposits, caused by incomplete combustion, form on the pot side and in the upper regions of the burner and reduce heat transfer to the surrounding space. Cokelike deposits, caused by cracking or condensation reactions in the pool of vaporizing oil, form on the pot bottom and tend to clog the oil inlet. Because both types of deposits form rapidly with cracked fuel oils, straight-run fuels are generally used.