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# Effect of Temperature and Air Rate on the Liquid Phase Oxidation of Cetane[1]

by ROBERT J. HARVEY 2) (Tulsa) and PAUL ZÜRCHER 3) (Lugano)

## Abstract

The optimum air rate at each temperature for the range 110° C to 150° C and the temperature coefficient of oxidation of cetane were investigated. For each temperature, an optimum air rate was attained beyond which no appreciable increase occurred in the rate of oxidation. The optimum rate was related empirically to the temperature by the equation: $\text{Log } D_L = 0.0212\,t - 3.15$. The rate of oxidation at optimum air rate conditions increases about 2.325 times for each 10° C. rise in temperature for the 110° C. to 140° C. range. An equation expressing the relationship between the reaction rate and the reciprocal of the absolute temperature is:

$$\text{Log } K = \frac{-5790}{T} + 15.1.$$

Generalizations regarding the trend of the data are:

1. Water and carbon dioxide formation increases with increasing temperature and air rates.
2. The ester content of the oxidized product increases slightly at higher temperatures.
3. Acid and saponification numbers have no direct relation to the yield of the oxidized product or the air rate.

Within the scope of this study, the following previous work is of specific interest:

KROEGER and KOLLER (6) oxidized one gram-mole of cetane with oxygen in a closed system at atmospheric pressure with a circulation rate of oxygen of eleven liters per hour at 120° C., 140° C. and 150° C. The average temperature coefficient of oxidation of cetane as calculated from oxygen absorption data is 2.29 for 120° C. to 140° C. and 3.02 for 140° C. to 150° C.

SALWAY and WILLIAMS (9) carried out the oxidation of cetane for twenty-four hours at 120° C. to 130° C. in a current of oxygen with 2 % of manganese stearate as a catalyst. Four per cent of unidentified volatile acids, carbon dioxide, formic and acetic acids were obtained. The rest of the reaction products consisted of about 70 % acidic substances and 30 % unchanged cetane. The acidic substances, after extraction with sodium hydroxide, consisted of a pale yellow oil, about 20 % of which was volatile with steam, and appeared to be principally hexanoic and nonanoic acids. The non-volatile portion was largely lactonic acids similar to those produced by the oxidation of stearic acid.

LARSEN, et al (7) oxidized cetane with oxygen at 110° C. at atmospheric pressure in a study on the oxidation characteristics of pure hydrocarbons.

HASS, et al (4) oxidized cetane with one-half mole of oxygen as air per mole of cetane at 2000 psig at 190° C., 250° C. and 300° C.

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ARDITTI (1) obtained a value of 1.96 for the temperature coefficient of oxidation of cetane over a temperature range of 100 $^0$ C. to 132 $^0$ C.

BALSBAUGH, et al (2) oxidized cetane with oxygen at 85 $^0$ C. at 760 mm. Hg. Also BALSBOUGH and ONCLEY (3) oxidized cetane with oxygen at 100 $^0$ C. and 105.1 $^0$ C. at 760 mm. Hg.

PARDUN and KUCHINKA (8) developed the following relationship from a study of the oxidation of Fischer-Tropsch slack wax.

$$\text{Log } D_L = 0.03\, t - 4.30$$

For optimum production of fatty acids the constant 4.30 is replaced by 4.60 in the above formula. The temperature coefficient of oxidation remains practically constant at 2.52 in the temperature range of 110 $^0$ C. to 140 $^0$ C.; above that range the value decreases appreciably. A similar form of the above relationship applies to different types of equipment.

From published data (2, 3, 7) on the oxidation of cetane with oxygen at atmospheric pressure, calculations were made illustrating the effect of temperature as shown in Table I.

### Table I

### Effect of Temperature on the Oxidation of Cetane

| Temperature Degrees Centigrade | a 5) | b 5) | $\frac{b}{a}$ | $\log \frac{b}{a}$ | $\frac{10^3}{T}$ | Activation Energy, Calories per gram-mol |
|---|---|---|---|---|---|---|
| 85 | 0.12 | 0.0023 | 0.01917 | — 1.718 | 2.80 | |
| 100 | 0.12 | 0.0086 | 0.0716 | — 1.14 | 2.681 | 25,900 |
| 105.0 | 0.16 | 0.023 | 0.1438 | — 0.84 | 2.645 | |
| 110 | 0.291 | 0.3028 | 1.041 | 0.018 | 2.610 | 19,400 6) |
| 4) 130 | 0.222 | 0.8214 | 3.70 | 0.568 | 2.480 | |

From the equations for each temperature, the times required for the same level of oxidation at different temperatures were calculated. By plotting the logarithm of the amount of oxygen absorbed per kilogram of cetane versus the ratio of contact times (time at the lower temperature divided by the time at the higher temperature) two straight lines were obtained for the temperature ranges 85 $^0$ C. to 105.1 $^0$ C. and 110 $^0$ C. to 130 $^0$ C. The line for the 85 $^0$ C. to 105 $^0$ C. temperature range indicates a decrease in ratio of contact times at successively higher levels of oxidation; the opposite being true for the 110 $^0$ C. to 130 $^0$ C. temperature range.

The apparatus used in this investigation consisted of an air-flow system, a reaction system and a product system.

In the air flow system (Fig. 1) a water column 125 cm. high and five cm. in diameter served as a pressure equalizer. The air entered the equalizer within nine cm. from the bottom. The surge tank (2), a 200 liter drum, smoothed out the air flow. An inclined manometer (3) measured the pressure differential across the restriction caused by the pinch clamp in the air line. The air was dried by passing it through a 25 cm column of silica gel (4).

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4) Data extrapolated by LARSEN et al (7).

5) The parameters a and b are obtained by plotting the oxidation data to the equation: $V^a = b\, t$, in which V = milliliters oxygen absorbed at normal temperature and pressure, and t = time, hours. The usual velocity constant, K, is represented by $\frac{b}{a}$

6) ARDITTI (1) obtained a value of 21,200 calories per gram-mol.

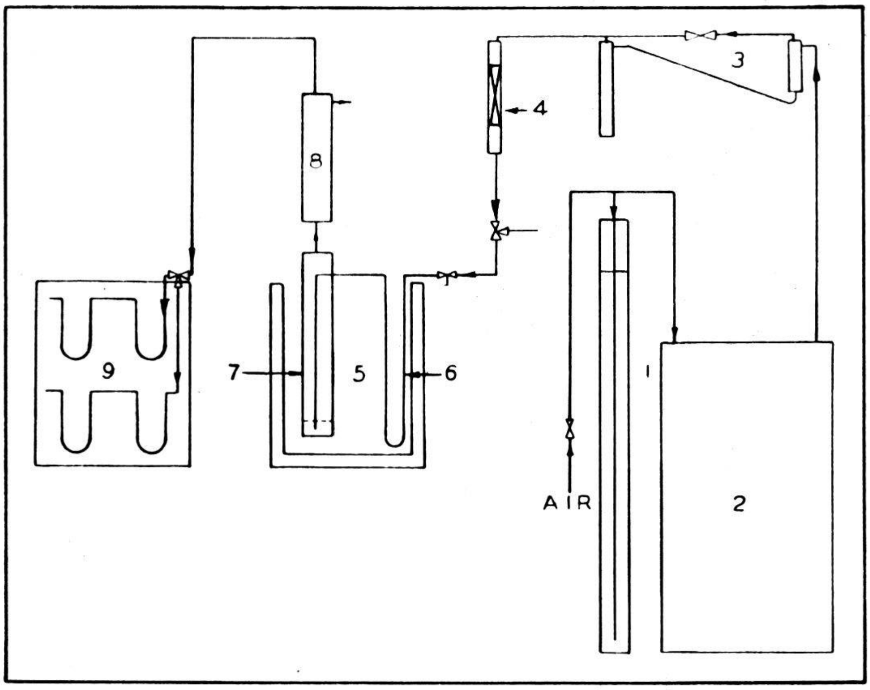

Fig. 1. Schematic Flow Diagram

1 - Pressure Equalizer; 2 - Surge Tank; 3 - Manometer; 4 - Silica Gel; 5 - Reaction System;
6 - Air Heater; 7 - Reaction Vessel; 8 - Condenser; 9 - Absorbers for Water and Carbon Dioxide

The reaction system (5) was submerged in an oil bath heated by a LoLag immersion heater. Temperature regulation was by means of a bimetallic controller with time relay.

The air was heated to the desired temperature by a U-tube (6) and was then dispersed by a porous plate at the bottom of the reaction vessel (7). The volatile reaction products were cooled in a condenser (8) and passed into U-tubes (9) where water and carbon dioxide were absorbed. The flow rate was controlled to ± 0.018 liter an hour per gram of cetane. The oil bath temperature varied ± 2 ° C. The air supply pressure fluctuated ± 1 cm water.

Practical grade cetane, as supplied by the Eastman Kodak Company was used without further purification. Fifty ml. of cetane were weighed into the reaction vessel (7) when the oil bath (5) was at the desired temperature. Air was admitted immediately and the rate adjusted by the pinch clamp on the inlet air line (1, 2, 3, 4). The stopcock leading to the absorbers was opened, and cooling water was admitted to the condenser (8).

One set of absorbers (9) was weighed intermittently in order to follow to some extent the course of the oxidation reaction. Acid numbers and saponification numbers were determined intermittently by withdrawing samples of 300—500 mg.

After the desired reaction time, the air flow was interrupted, the stopcock to the absorption tubes closed, and the reaction vessel removed from the bath and cooled. Acid and saponification numbers of the final product were determined. The reaction products were shaken with anhydrous calcium chloride and filtered to remove water, and the amount of water determined. The volume and density of the reaction product were recorded. The oxidized sample was contacted with cold, concentrated sulfuric acid, and the extract layer was water-washed, dried and its volume and density recorded. The volume was corrected for the amount withdrawn during the run. This purified raffinate was found to be unreacted cetane. The volume times the density of the purified raffinate layer divided by the weight of the original charge yielded the per cent of unoxidized cetane. The amount of entrainment of cetane was assumed to be negligible.

A measure of the ester content was obtained by subtracting the acid number from the saponification number. It is to be understood that these two numbers reveal nothing of the nature of the compounds such as alcohols, aldehydes etc. The amounts of carbon dioxide and water formed were recorded as mg. per hour per gram of sample. A summary of test data is shown in Table II.

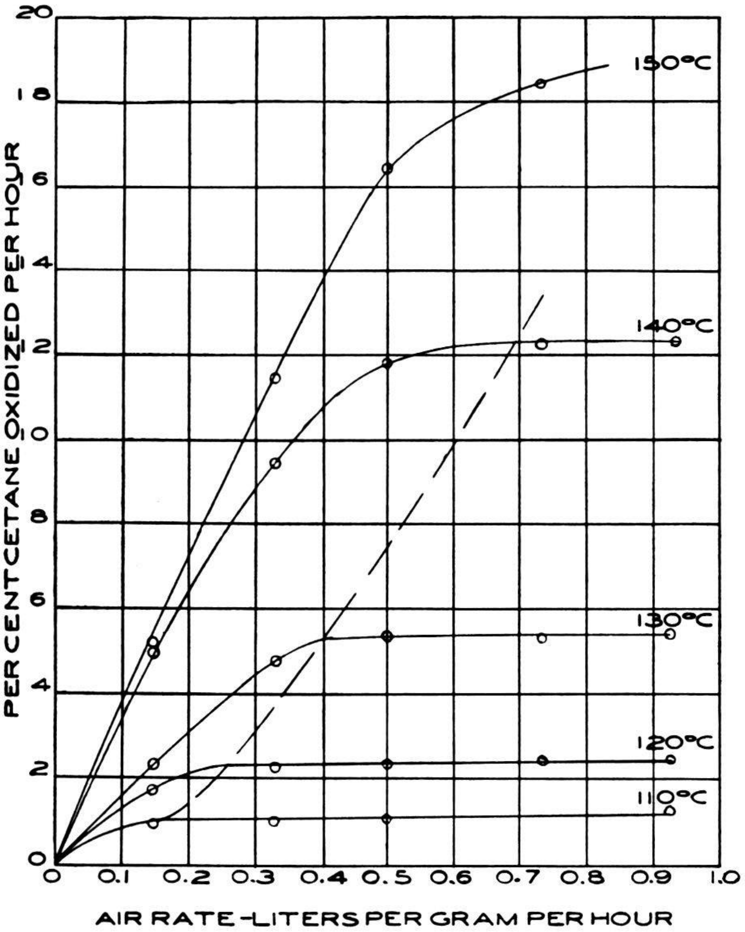

Fig. 2. Optimum Air Rate

Optimum Air Rate — Figure 2 reveals that, as the air rate is increased, the oxidation rate rises to a maximum and shows no appreciable increase thereafter. The air rate giving the maximum rate of oxidation at any particular temperature was designated the optimum air rate. The optimum air rates for each temperature are shown by the dashed line in Figure 2. The data of KROEGER and KOLLER (6) when plotted on the same basis, are in good agreement with the experimental curves.

In order to express concisely the relationship between optimum air rate and reaction temperature, a semi-logarithmic plot of the optimum air rate vs. temperature, ranging from 110 ° C. to 140 ° C. was made. By the method of averages, the following equation was derived:

$$\text{Log}\, D_L = 0.0212\, t - 3.15$$

## Table II Summary of Data

| Run Number | Temperature, degrees Centigrade | Air Rate, liters per gram per hour | Time hours | Acid Number mg. KOH per gram | Saponification Number mg. KOH per gram | Ester Content, mg. KOH per gram | $CO_2$ mg. per hour per gram | $H_2O$ mg. per hour per gram | Per Cent Cetane Oxidized per hour |
|---|---|---|---|---|---|---|---|---|---|
| A-1 | 110 | 0.150 | 30 | 43.2 | 78.0 | 34.8 | 0.21 | 1.57 | 0.95 |
| A-2 | | 0.328 | 30 | 44.0 | 79.2 | 35.2 | 0.59 | 4.32 | 1.02 |
| A-3 | | 0.500 | 30 | 45.3 | 80.8 | 35.5 | 1.01 | 7.53 | 1.10 |
| A-5 | | 0.929 | 30 | 46.1 | 82.0 | 35.9 | 1.58 | 11.61 | 1.30 |
| | | | | | | | | | |
| B-1 | 120 | 0.150 | 24 | 47.1 | 83.6 | 36.5 | 0.31 | 2.36 | 1.76 |
| B-2 | | 0.328 | 20 | 52.0 | 89.0 | 37.0 | 0.68 | 4.97 | 2.30 |
| B-3 | | 0.500 | 20 | 52.6 | 89.8 | 37.2 | 0.96 | 7.20 | 2.39 |
| B-4 | | 0.739 | 20 | 52.7 | 90.0 | 37.3 | 1.42 | 10.71 | 2.43 |
| B-5 | | 0.929 | 20 | 53.2 | 91.2 | 38.0 | 1.60 | 11.80 | 2.50 |
| | | | | | | | | | |
| C-1 | 130 | 0.150 | 20 | 49.0 | 86.2 | 37.2 | 0.38 | 2.89 | 2.36 |
| C-2 | | 0.328 | 12 | 53.7 | 93.6 | 39.9 | 0.75 | 5.48 | 4.82 |
| C-3 | | 0.500 | 9 | 47.5 | 84.5 | 37.0 | 1.14 | 8.51 | 5.36 |
| C-4 | | 0.739 | 9 | 47.2 | 84.6 | 37.4 | 1.54 | 10.41 | 5.32 |
| C-5 | | 0.929 | 9 | 49.0 | 87.0 | 38.0 | 1.70 | 12.67 | 5.47 |
| | | | | | | | | | |
| D-1 | 140 | 0.150 | 10 | 52.0 | 92.3 | 40.3 | 0.41 | 3.06 | 5.00 |
| D-2 | | 0.328 | 7 | 133.3 | 175.5 | 42.2 | 0.86 | 6.43 | 9.47 |
| D-3 | | 0.500 | 6 | 150.2 | 191.8 | 41.6 | 1.26 | 9.46 | 11.85 |
| D-4 | | 0.739 | 6 | 153.0 | 195.8 | 42.8 | 1.66 | 12.77 | 12.30 |
| D-5 | | 0.929 | 6 | 155.1 | 198.0 | 43.9 | 1.83 | 13.60 | 12.46 |
| | | | | | | | | | |
| E-1 | 150 | 0.150 | 12 | 132.0 | 178.0 | 45.0 | 0.46 | 3.50 | 5.23 |
| E-2 | | 0.328 | 6 | 138.0 | 184.3 | 46.3 | 0.88 | 6.47 | 11.52 |
| E-3 | | 0.500 | 4 | 135.3 | 181.2 | 45.9 | 1.26 | 9.39 | 16.50 |
| E-4 | | 0.739 | 4 | 151.8 | 198.4 | 46.6 | 1.71 | 12.67 | 18.52 |

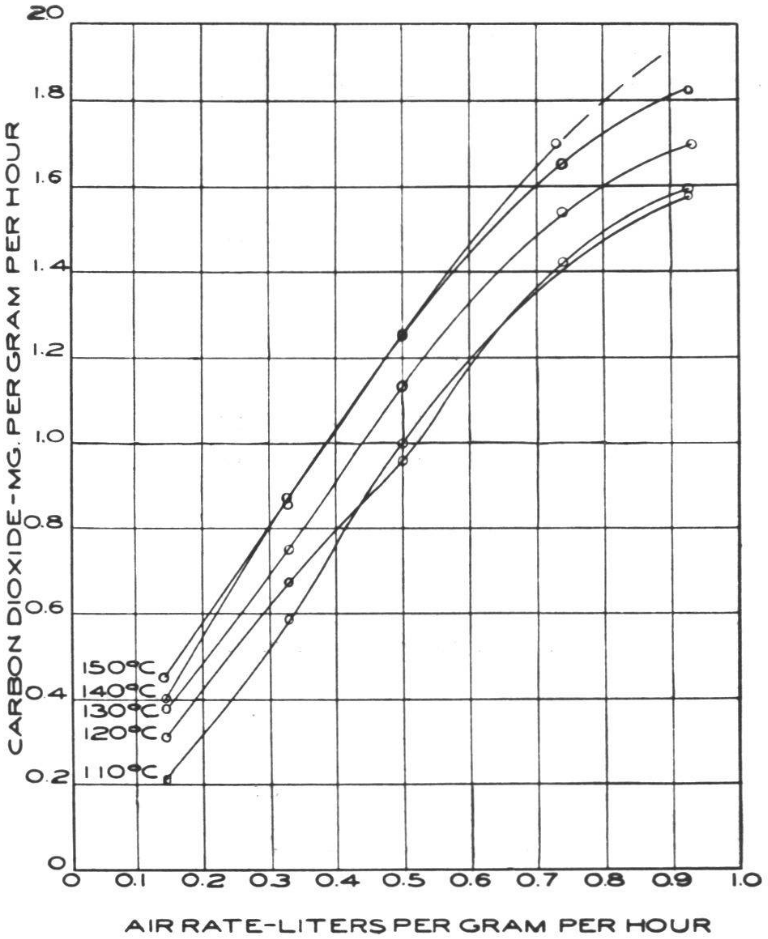

Fig. 3

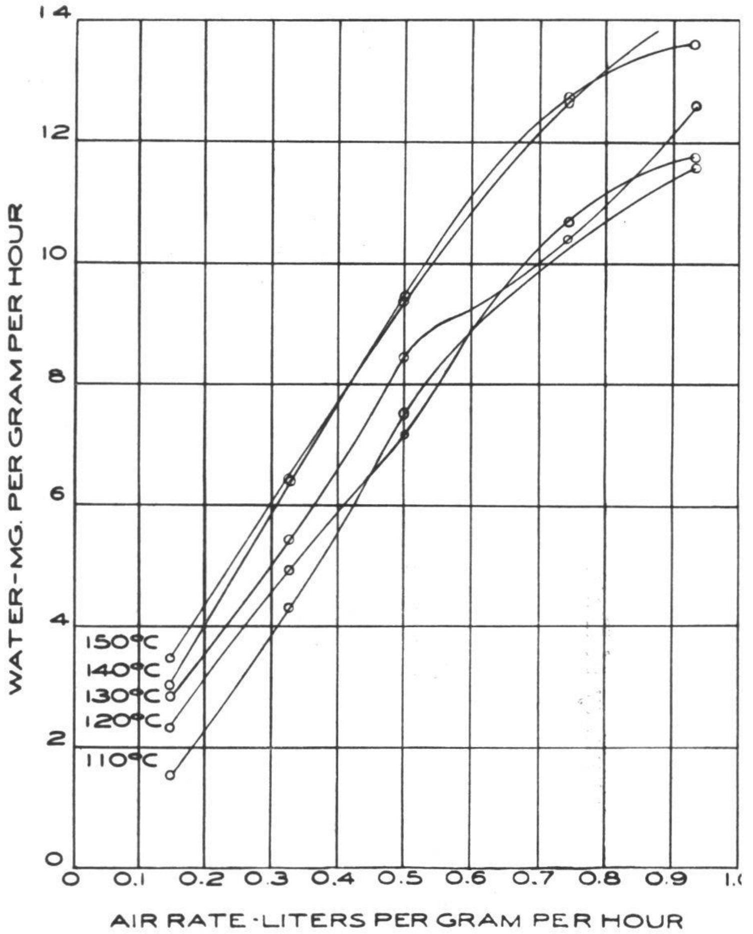

Fig. 4

By interpolation, the optimum air rate at 150 ° C. is 1.07 liters per gram per hour. The above relationship yields higher optimum rates for a given temperature than those developed by PARDUN and KUCHINKA (8) indicating that the higher paraffin homologs oxidize more readily.

Reaction Rates — The oxidation rate at the optimum air rate was determined for each temperature. Applying the data to the integrated form of the Arrhenius equation,

$$\mathrm{Log}\,K = \frac{E}{2.303\,R}\,\frac{1}{T} + C$$

yielded a value of E of 26,500 calories per gram-mol which is higher than that indicated in Table I, using pure oxygen as an oxidizing medium. The constant, C, equals 15.1. For each ten degrees rise in temperature, the oxidation rate increased an average of 2.325 times.

Ester and Carbon Dioxide Formation — The values representing water and carbon dioxide formation in Table II, were graphed against the air rates in Fig. 3 and 4. No exact relationship was developed. Generally, water and carbon dioxide formation increased with an increase in temperature and air rate, thus indicating a tendency to over-oxidation at higher temperature and air rates. HICKS-BRUUN et al (5) present three classes of oxidation reactions as follows:

Class I. No gaseous reaction products are formed.

$$R(CH_2)R' + \tfrac{1}{2}O_2 \rightarrow R(HCCH)R'$$

Class II. Water is the only gaseous reaction product.

$$R(CH_2)R' + O_2 \rightarrow R(CO)R' + H_2O$$
$$R(C_2H_4)R' + 1\tfrac{1}{2}O_2 \rightarrow RCHO + R'CHO + H_2O$$

Class III. Water formation is accompanied by the liberation of carbon dioxide, carbon monoxide, or low-membered paraffin, olefin, or acetylene hydrocarbons.

$$R(C_2H_6)R' + 3O_2 \rightarrow CO_2 + 2H_2O + RCHO + R'CHO$$
$$R(C_2H_6)R' + 4O_2 \rightarrow CO_2 + 2H_2O + RCOOH + R'COOH$$

In the Class III equations, two molecules of water are formed for every molecule of carbon dioxide; therefore, the water formed corresponding to the carbon dioxide can be calculated. The amount of water remaining results from Class II reactions. On this basis the data for Table III were calculated.

**Table III**

**Per Cent of Water Formed in Class II Reactions**

| Run Number | Water Formed in Class II Reactions, mg. per gram per hour | Per Cent of Water Formed in Class II Reactions |
|---|---|---|
| A-1 | 1.33 | 84.7 |
| A-2 | 3.66 | 84.7 |
| A-3 | 6.39 | 84.8 |
| A-5 | 9.83 | 84.5 |
| B-1 | 2.01 | 85.2 |
| B-2 | 4.20 | 84.5 |
| B-3 | 6.12 | 85.1 |
| B-4 | 9.11 | 85.0 |
| B-5 | 10.00 | 84.8 |
| C-1 | 2.46 | 85.2 |
| C-2 | 4.64 | 84.5 |
| C-3 | 7.23 | 84.6 |
| C-4 | 8.68 | 83.3 |
| C-5 | 10.76 | 85.0 |
| D-1 | 2.60 | 85.0 |
| D-2 | 5.46 | 84.5 |
| D-3 | 8.04 | 85.0 |
| D-4 | 10.90 | 85.5 |
| D-5 | 11.54 | 85.0 |
| E-1 | 2.98 | 85.1 |
| E-2 | 5.48 | 84.6 |
| E-3 | 7.97 | 85.0 |
| E-4 | 10.75 | 85.0 |

The per cent of water formed in the Class II reactions remained practically constant at 85 per cent. HICKS-BRUUN et al (5) found that about 96 per cent of the water was formed in the Class II reactions for short periods of time, falling off to about 85 per cent for longer periods.

Ester Formation — Acid numbers and saponification numbers could not be correlated with any of the other variables in the reaction, but in general they increase with an increase in the oxidation yield. Ester contents, as shown in Table II, increase slightly at higher temperatures. Therefore, it is not possible to utilize the acid number or saponification number as the sole criterion of the extent of oxidation.

## NOMENCLATURE

$C$ = Constant in the Arrhenius Equation
$D_L$ Optimum air rate, liters per gram of original sample per hour

$E$ = Activation energy, calories per gram-mol
$K$ = Oxidation rate, per cent cetane oxidized per hour
$R$ = Gas constant, calories per gram-mol per °K
$T$ = Temperature, °K
$t$ = Temperature, °C

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