

EVALUATION OF HYDROCARBON EXPLOSION LIMIT IN A CHEMICAL PLANT

Yasuhiko Ohta and Masahiro Furutani
Nagoya Institute of Technology, Nagoya, Japan

1. INTRODUCTION

Acetyl acid is a basic material of paints and synthetic textile binders. Acrolein (acrylic aldehyde, $\text{CH}_2=\text{CHCHO}$) is one of the most important intermediates in the process producing acetyl acid from propylene. Acrolein is formed through a low-temperature propylene oxidation. Reactor outlet temperature and pressure are about 235°C and 2 atm, where oxygen coexists with acrolein. When a higher production capacity of the plant are desired, higher temperature and/or pressure will be required, and apprehensions of cool flame onset could come out in consequence. If the cool flame develops to the final hot-flame stage an explosion hazard of the plant would be caused.

Safety operation temperature/pressure conditions should be evaluated to prevent low-temperature hydrocarbon oxidation from exploding chemical plants. The circumstances are quite similar to knocking phenomenon of premixed charge in spark-ignition internal combustion engines. Ignition caused in a rapid-compression machine will be informative for this evaluation. Cool-flame ignition-delay time τ can be measured for acrolein mixtures, and its temperature and pressure dependence and inert-gas dilution effect on the ignition delay will be also estimated by piston-compression experiments of the mixtures. Safe operation of real plants can be accomplished only with residence times shorter than the estimated time based on the conditions at the reactor outlet and transport pipe line connected to the next reaction stage.

2. EXPERIMENTAL

Premixed piston-compression-ignition experiments were carried out to measure ignition delay (induction time) up to the cool-flame appearance and final hot-flame onset, using a rapid-compression machine with 65-mm bore and 140-mm stroke. Details of the rapid-compression machine is described elsewhere ^{1, 2, 3}. The fuel used was reagent-grade acrolein, and the oxidizer was pure air (dew point: not higher than -70°C) or O_2/N_2 mixed gases. A vaporized fuel and an oxidizer were mixed in a separate vessel, and the mixture was introduced into the cylinder. The recorded pressure at the end of compression stroke gave us the compression temperature with an aid of known values of compression ratio, initial temperature and pressure of the mixture at the start of compression stroke.

Associated with pressure history, blue (350 ~ 520 nm) and red (590 ~ 640 nm) visible light emissions were observed through the quartz windows during and after the compression to detect each of the cool-, blue- and final hot-flame appearances using combinations of color-glass filter and 1P28 photomultiplier. Cool-, blue-, and hot-flame identification scheme adopted here, together with spectral sensitivity of photomultiplier and transmissivities of filters is described in Ref. 4. Temperature and pressure ranges prepared by piston compression were 200 ~ 350 $^\circ\text{C}$ and 5 ~ 15 atm.

The typical operating temperature and pressure conditions of a real plant at the first reactor outlet are supposed to be 230 ~ 240 $^\circ\text{C}$ and 1.7 ~ 2.1 atm. An example of reacting gas composition at the position is shown in Table 1.

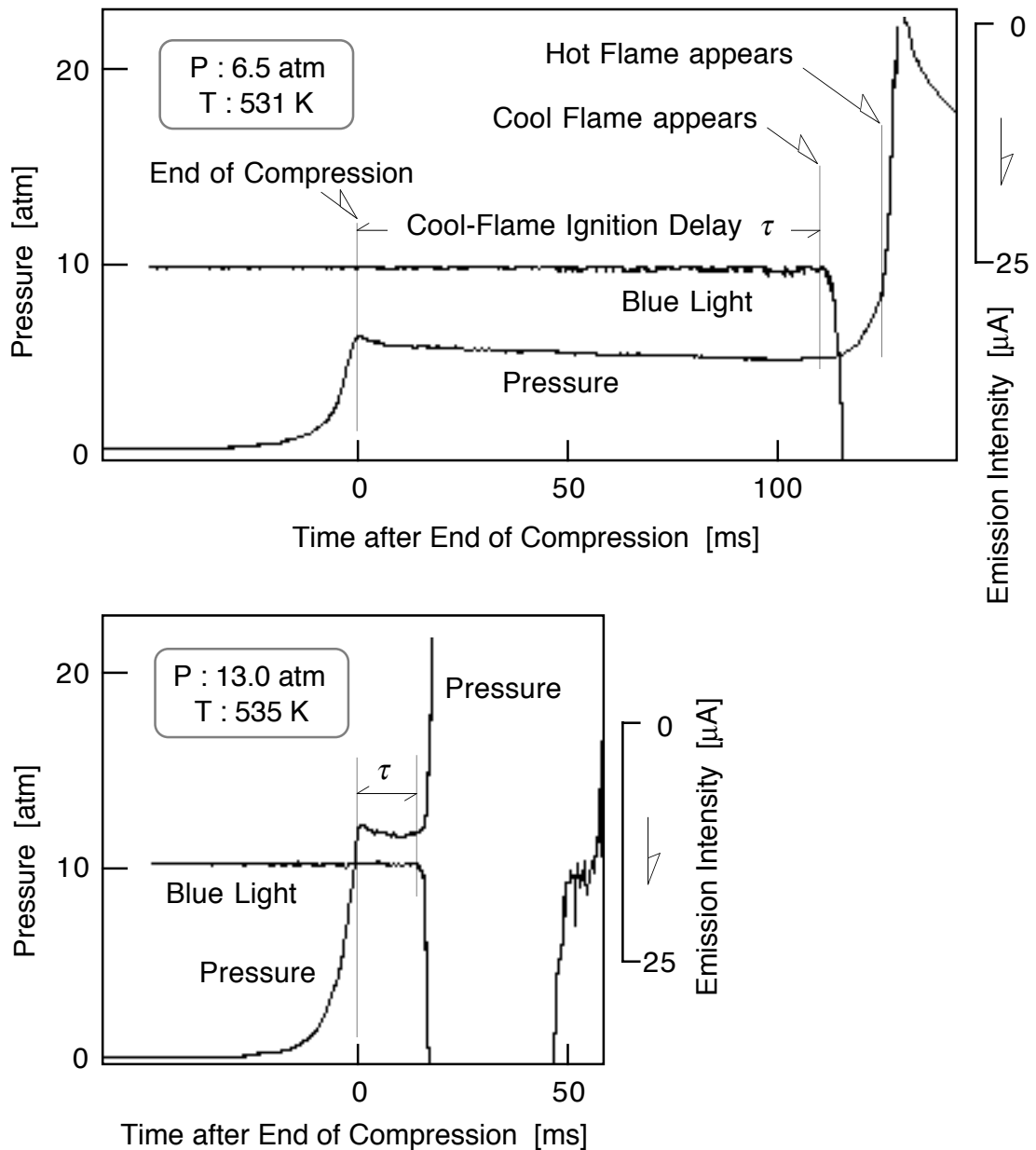


Figure 1. Piston-compression ignition processes of a rich acrolein/air mixture under pressures 6.5 and 13 atm and an identical compression temperature, shown by the pressure and blue-light emission histories up to the final hot flame.

An equimolar mixture of acrolein and oxygen was selected as the first representation, taking the other inflammable substances than acrolein into consideration; this mixture corresponds to an equivalence ratio 3.5, which is capable to oxidize the fuel acrolein just until $3\text{CO} + 2\text{H}_2$. We call hereafter this equimolar mixture of acrolein and oxygen "Reactant". At the beginning we supplied the oxygen as a part of pure air, so that the composition of typical mixture to be tested was: 17.36 acrolein, 17.36 oxygen, 64.46 nitrogen, and 0.82 argon, i. e. the "Reactant" was diluted with slightly-argon-contained nitrogen.

Table 1. Typical constituent of a real plant at the first reactor outlet

Acrolein	6.8
Acrylic acid	0.64
Formaldehyde	0.35
Propylene	0.18
Carbon monoxide	0.42
Carbon dioxide	0.88
Water vapor	34
Oxygen	4.3
Nitrogen	52
Others	0.4

3. RESULTS AND DISCUSSION

3.1 Temperature and Pressure Dependence for Cool-Flame Appearances

Cool flame ignition delay time τ was measured for the rich acrolein/air mixtures having equivalence ratios of 3.0 to 4.0. Ignition under the compression pressure 5 to 20 atm is a favorite

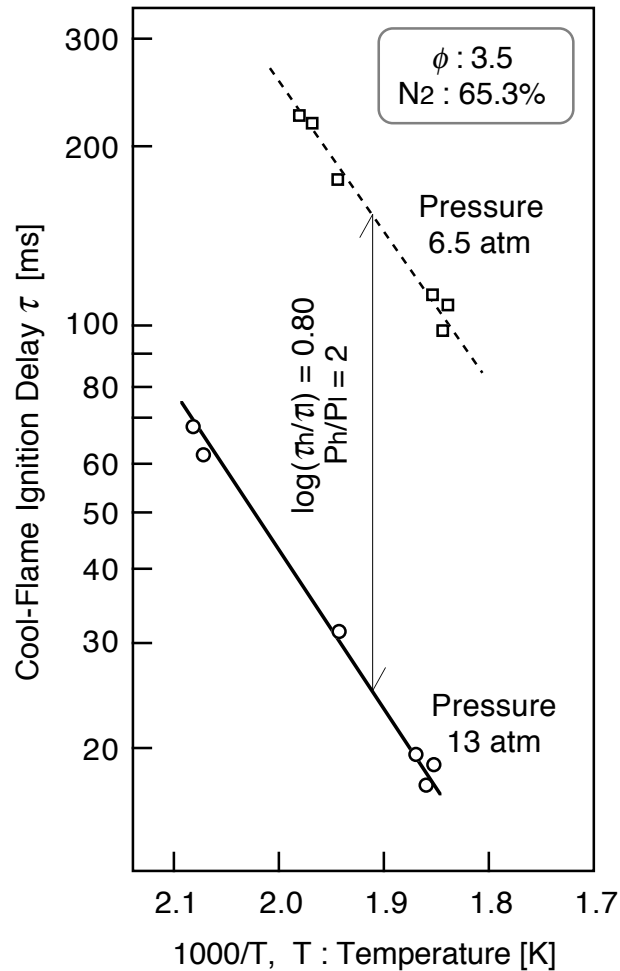


Figure 2. Arrhenius plots for the cool-flame ignition delay of a rich acrolein/air mixture for pressures 6.5 and 13 atm. Estimation of temperature and pressure dependence for cool-flame appearances.

subject of rapid-compression machines, but not at lower pressure conditions. The cool-flame ignition in the real plant cases close to the atmospheric pressure should be estimated by extrapolation of ignition behaviors obtained under 6.5 and 13 atm. Two fixed pressure conditions, 6.5 and 13 atm, were programmed to estimate the pressure dependence on the cool-flame ignition.

Piston-compression ignition processes under each pressure mentioned above is illustrated in Figure 1 with the pressure and blue-light emission histories up to the final hot flame. The compression temperature is identical between the two. Light-emission traces swing downward when the intensity increases. Blue-light emission and the pressure recovery due to heat release start simultaneously whereupon cool flame appears.

The Arrhenius plots for the cool-flame ignition delay are shown in Figure 2 for both pressure conditions. Temperature coefficient for the preflame reaction or its apparent activation energy can be estimated from the fitted-line gradients of the ignition-delay plots. Quite similar gradients have been given for the two pressure condition. Pressure dependence on the ignition delay is calculated from the disparity between the two group of the plots. No distinct difference could not be found in ignition delays among the mixtures with equivalence ratios between 3.0 and 4.0.

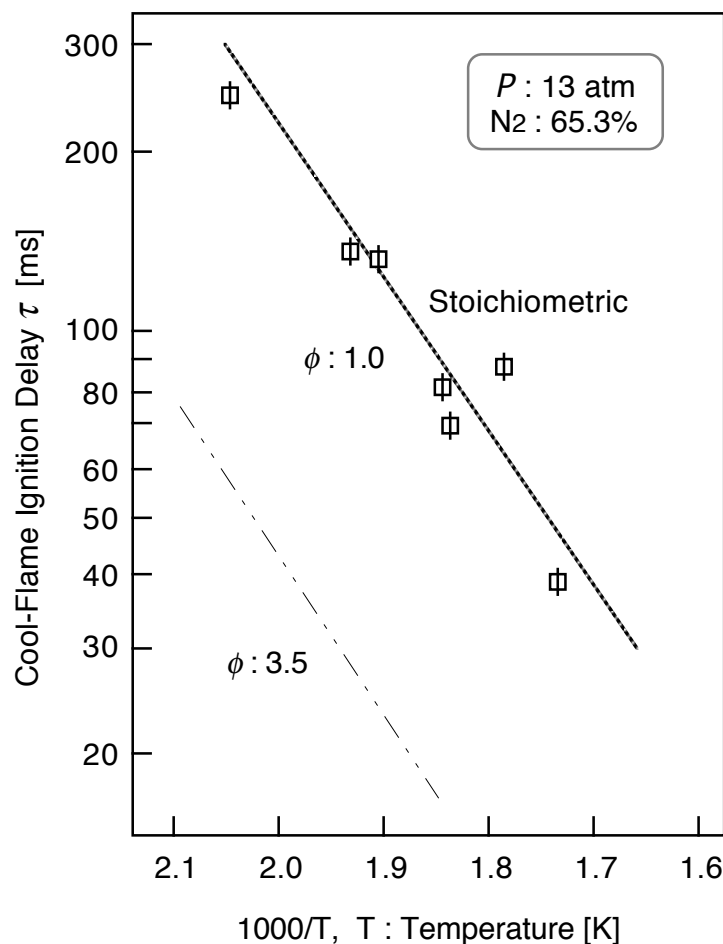


Figure 3. Arrhenius plots for the cool-flame ignition delay of a stoichiometric acrolein/air mixture under a pressure 13 atm.

An empirical Arrhenius expression for the overall reaction has been obtained herewith resulting in an apparent activation energy of 11.8 kcal/mol and pressure index 2.7:

$$\tau = 3.012 \times 10^{-4} P^{-2.7} \exp(11.8/RT) \text{ [s]}$$

here, P : pressure [atm], T : temperature [K] and R : universal gas constant of 1.986×10^{-3} [kcal/mol K].

The piston-compression ignition delay for the stoichiometric acrolein/air mixture is also measured. Figure 3 is the result. Contrary to our expectations, the ignition delay is longer than the previous rich case. For the popular hydrocarbons, such as n-heptane, iso-octane and n-butane, slightly rich condition around equivalence ratio 1.1 would show the most explosive tendency. Ignition-delay data scatter widely in this figure. However, as concerns the activation energy, it could not differ greatly from the former value 11.8 kcal/mol. The equivalence ratios higher than 3 is too rich to obtain hot-flame ignition for the popular hydrocarbons.

No ignition could be obtained for the stoichiometric acrolein/air mixture under the pressure condition lower than 7 atm. By using rapid compression machine ignition delay longer than 500 ms cannot be accomplished because of the heat losses from the walls. With this mixture strength we could not determine the pressure dependence for the ignition delays.

3.2 Effect of Inert Gas Dilution

We have to elucidate the effect of inert gas content in the reacting gases. In other words, the selected mixture as the first representation had another amount compared with reacting gases in the real plant related to the species other than "reactant". Up to here, the pure air was used as an oxidizer, where the nitrogen was the only inert species. Water vapor and carbon dioxide are also included in the gases coming out from the first reactor as shown in Table 1, though the amount of carbon dioxide is very small. It has not been clearly known whether the water vapor would participate positively the low-temperature preflame reactions. For the n-butane low-temperature ignitions, water-vapor addition slightly influences on the preflame reactions⁵. The water vapor is assumed herewith, similar to the nitrogen, to have no chemical effect except the diluent effect or heat-capacity-increasing effect for the cool-flame appearance. We call here these inert species "Diluent". In the case of equimolar mixture of acrolein and oxygen which supplied by a part of air, the Diluent/Reactant ratio was 1.88, where the argon is counted among the inert species.

We programmed the other two Diluent/Reactant ratios (D/R) to be 4.77 and 10.53, in which the reactant contents were reduced to be a half and a quarter. The "Reactant" was fixed to be the acrolein-oxygen equimolar mixture; acrolein or oxygen fraction is 8.67 and 4.34 per cent respectively. Using these two mixtures, piston-compression ignitions were caused and the cool-flame ignition delays were measured. Temperatures at the end of compression were varied under a fixed pressure condition of 13 atm. The results are illustrated in Figure 4. We can obtain the diluent index to be 1.4 with no modification of activation energy.

The final empirical Arrhenius expression could be expressed as follows, in which the dilution effect taking into account:

$$\tau = 1.056 \times 10^{-4} (\text{Diluent/Reactant})^{1.4} P^{-2.7} \exp(11.8/RT) \text{ [s]}$$

However, calculated ignition delays by this empirical expression for the first mixture having the D/R ratio of 1.88 slightly differ from the measured delays as shown with the dotted line in the figure. For this discrepancy we did not modify the pre-exponential factor, coefficients and

indexes, because the real-plant condition is close to the cases with higher Diluent/Reactant ratios.

3.3 Safety Limit Estimation for Real Plant

In a case of a real plant the Diluent/Reactant ratio can be considered to be 7.5 for an example listed in Table 1. For the typical operating condition, 235°C and 2 atm with a D/R of 7.5, the calculated ignition-delay time is 32.7 s. At present the residence time allocated from the first-reactor outlet to the next reaction stage through transport pipe line is 4 s. It can be seen that a relatively reasonable safety margin, $32.7/4 \cong 8$, is given for this plant operation. The operation at 250°C under the pressure condition of 2.2 atm, for example, will be done with an estimated ignition delay of 18.1 and a safety margin less than 5. Less margin will yield not only danger for explosion hazard of the plant but also less expected products and more unexpected constituents of the gases due to the preflame reactions continuing during transfer process.

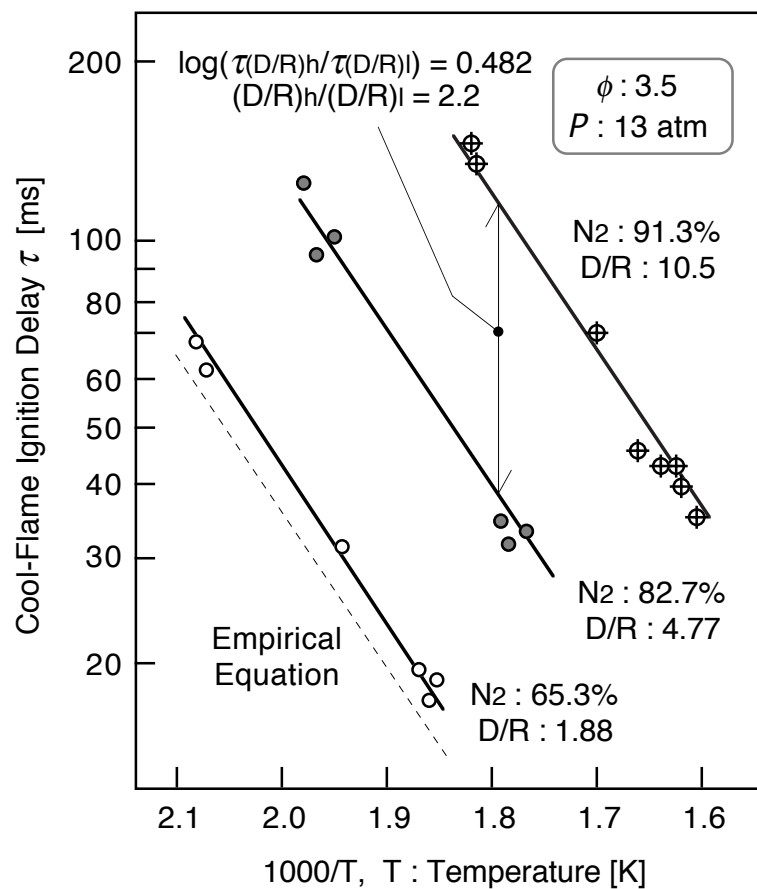


Figure 4. Estimation of inert-gas dilution effect. D/R is Diluent/Reactant ratio; Reactant is acrolein/oxygen equimolar mixture and Diluent is nitrogen.

4. CONCLUDING REMARKS

Cool flame ignition delay time τ has been measured using a rapid-compression machine for rich acrolein/O₂/N₂ mixture having an equivalence ratio of 3.0 to 4.0 modeled on a real plant operation. Temperature and pressure dependence, and inert-gas dilution effect on the ignition delay were also estimated by piston-compression experiments of the mixture.

An empirical Arrhenius expression was obtained herewith resulting in an apparent activation energy of 11.8 kcal/mol and pressure index 2.7:

$$\tau = 1.056 \times 10^{-4} (\text{Diluent/Reactant})^{1.4} P^{-2.7} \exp(11.8/RT) \text{ [s]}$$

here, P : pressure [atm], T : temperature [K] and R : universal gas constant of 1.986×10^{-3} [kcal/mol K]. The "Reactant" was an acrolein/oxygen equimolar mixture with an equivalence ratio of 3.5 and "Diluent" was nitrogen for deriving the empirical expression.

In a real plant the mixture is diluted by water vapor as well as nitrogen. Water vapor can be counted among the diluent. For a present typical operating condition, a reasonable safety margin can be recognized. Limits of safe operation condition can be determined, with an appropriate safety margin, by comparing a cool-flame ignition delay τ and residence time of gases at the reactor outlet and transport line.

Rapid-compression machine is a useful tool for evaluating safety operation conditions of chemical oxidation reactors, though its experimental pressure range is higher and cool-flame ignition delay is two or three digits shorter than the operation conditions of real chemical plants.

5. REFERENCES

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