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Kinetics of Soot Formation in a Flow System Simulating the Lower Part of a Laminar Diffusion Flame*

By

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The conversion of fuel hydrocarbons into soot in a flow system simulating the lower part of a diffusion flame was investigated. The soot formation was assumed to consist of the decomposition of the fuel into fragment hydrocarbons, and the polymerization of the fragment hydrocarbons into pre-soot hydrocarbons. The pre-soot hydrocarbons are polycyclic hydrocarbons which form soot particles by further polymerization and condensation. These reaction processes were formulated by a set of differential equations on assuming the reactions are first order and reversible. The rate constants of the reactions and equilibrium constants between hydrocarbons were estimated. The rate constant of the decomposition ranged 7 to 50 sec⁻¹, and increased with increases in the reaction temperature and in addition of oxygen. The rate constant of the polymerization was approximately zero at a reaction temperature of 840°C, and increased with an increase in temperature. It increased with addition of oxygen to a maximum value of 2.8 sec⁻¹ at an oxygen ratio of 0.05 and then decreased, at 955°C. The addition of oxygen had little effect on the equilibrium constants which decrease with an increase in temperature i.e. the reverse reactions can be neglected at high temperatures. The equilibrium constant between fuel and fragment hydrocarbons was 0.5 at 840°C and nearly zero at 955°C. The equilibrium constant between fragment and pre-soot hydrocarbons was 4.0 at 905°C and 1.0 at 955°C.

Introduction

In an earlier paper¹⁾ the distribution of soot particles in laminar diffusion flames of petroleum gas was measured by a light-scattering technique. Intensive formation of soot particles was observed in a narrow zone in the lower part of the flame where the gas temperature was relatively low and a little air was intermixed.

The present work was undertaken to study the accompanying reaction and estimate the rate and equilibrium constants for the reaction. The conversion of fuel hydrocarbons into soot in a flow system simulating the lower part of a diffusion flame is investigated. The components in the mixture of fuel and oxidant are determined

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with gas chromatography after passing at various rates through the reaction tube kept at some temperatures of about 900°C. Then, the relative amount of carbon atoms distributed among the reaction products is calculated.

The soot is assumed to form by condensation of polycyclic aromatic radicals resulting from the polymerization of smaller hydrocarbon-radicals²⁾. These smaller radicals, such as $\text{CH}_3\cdot$ and C_2H_2 , are derived from the fuel hydrocarbons by decomposition reaction. Based on this assumption, the soot-forming reaction can be presumed to consist of the decomposition reaction of the fuel hydrocarbons into fragment hydrocarbons and the polymerization reaction of the fragment hydrocarbons into the polycyclic hydrocarbons. Rate constants of these reactions and equilibrium constants between the hydrocarbons are estimated.

Experimental

The fuel used was 95% pure liquid propane the impurities being chiefly *n*- and *i*- butanes. The fuel gas was diluted by nitrogen gas, and mixed with a small amount of oxygen gas or nitrogen-oxide gas as oxidant. Nitrogen-oxide gas was prepared by reduction of nitric acid with copper; gas-chromatographic and infrared-spectroscopic analyses showed that the gas was mixture of nitrogen-monoxide (55%) and dinitrogen-oxide (45%).

Gas mixture of fuel and oxidant was introduced into the reaction tube, which is a refractory porcelain tube having an inner diameter of 4 mm and heated in an

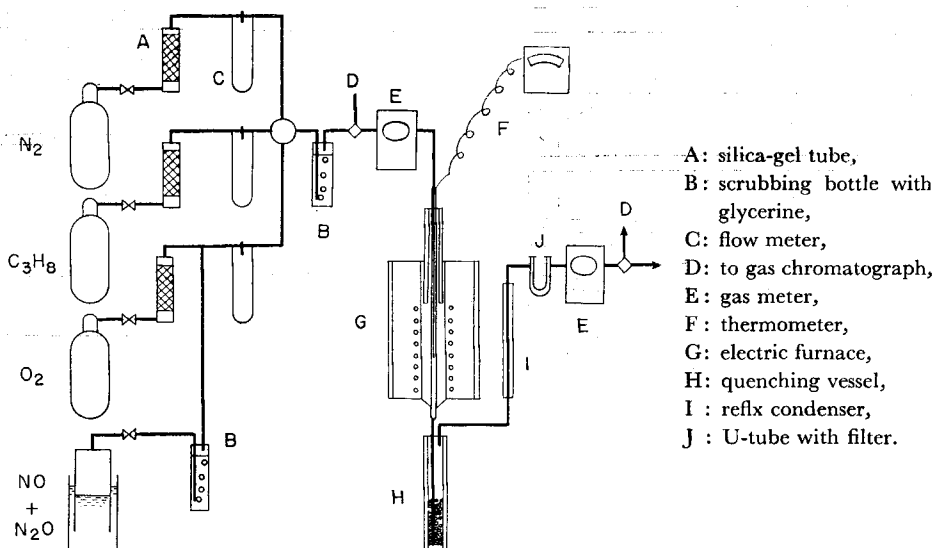


Fig. 1. Schematic arrangement of the apparatus.

electric furnace at a constant temperature of 840°C, 905°C or 955°C (Fig. 1). The flow rate was controlled to give reaction times ranging from 0.06 sec to 1.0 sec. After passing the reaction tube, the mixture was introduced to the bottom of a quenching vessel which is a metal cylinder being chilled with ice water circulating through the pipe twining round the cylinder. Reaction products with higher boiling point, including H₂O, condense and stay in glycerine film on glass beads packed in the vessel. The gaseous product was analyzed with gas chromatography. The individual components were H₂, O₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₆, C₄H₈, and C₄H₁₀.

Temperature in the reaction tube was measured by a thermocouple fixed at the center of the tube. The indication of the thermometer was changed as shown in Fig. 2 when the fuel mixture flowed into the tube. As there were occurring exothermic and endothermic reactions, it was rather hard to define a reaction temperature. Therefore, the initial temperature at the moment when the fuel mixture began to flow was used to represent a reaction temperature.

Figure 3 to 6 show distributions of carbon atoms from fuel hydrocarbons to the reaction products. The term "pre-soot" in figures means high-boiling point hydrocarbons which were condensed in the quenching vessel. The major part of the condensed substance trapped in the quenching vessel could be extracted with cyclohexane. Average molecular weight of the extract determined with cryoscopy

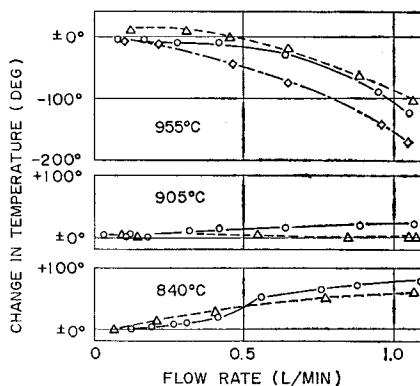


Fig. 2. Changes in temperature from initial temperatures of 840, 905 and 955°C at the center of the reaction tube flowing the mixtures of fuel (37.6%) with nitrogen (62.4%) (\diamond), with nitrogen (50.8%) and oxygen (11.6%) (\circ), and with nitrogen (44.9%) and oxygen (17.5%) (\triangle).

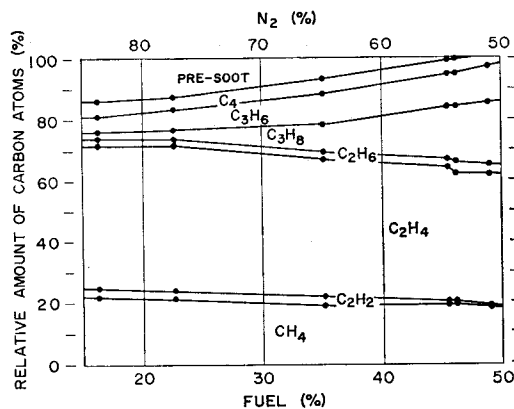


Fig. 3. Relative amount of carbon atoms distributed among the products from mixtures of fuel and nitrogen, through the reaction for 0.06 sec at an initial temperature of 955°C.

ranged from 170 to 250. Elution analysis with ultraviolet spectrometry³⁾ showed that the extract contained such aromatic hydrocarbons as benzene, naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene, 1:2-benzanthracene and chrysene. As these polycyclic hydrocarbon-molecules must be derived by quenching from the aromatic radicals which form soot particles by polymerization followed by condensation, they can be called pre-soot hydrocarbons.

Some fragment hydrocarbons, such as CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 , may be assumed to form through quenching from the small radicals such as CH_3 , etc.. These fragment hydrocarbons including small radicals would be produced by decomposition of the fuel hydrocarbons, and they would be polymerized to form molecules or radicals of polycyclic aromatic hydrocarbons, i.e., pre-soot hydrocarbons. The fuel decomposes rapidly, whereas the pre-soot hydrocarbons are formed slowly as shown in Fig. 4, so that the amount of carbon atoms shared by the fragment hydro-

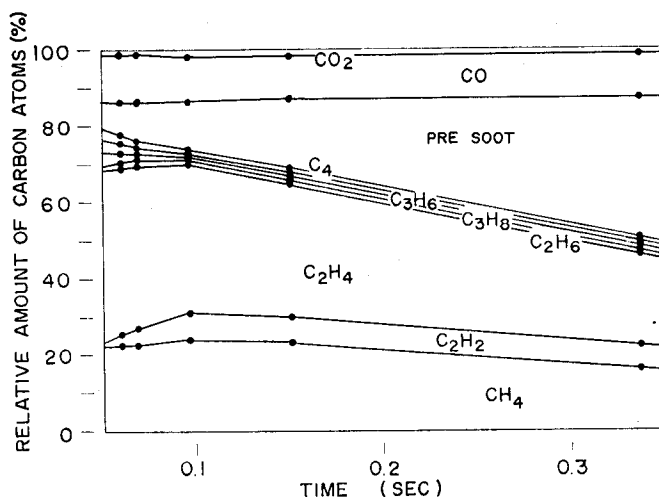


Fig. 4. Relative amount of carbon atoms distributed among the products from a mixture of fuel (37.6%), nitrogen (50.8%), and oxygen (11.6%), through the reaction at an initial temperature of 955°C .

carbons increases with time to a maximum at a point, and then decreases more and more slowly to an equilibrium.

The addition of the oxidant accelerates the formation of pre-soot hydrocarbons, as well as the decomposition of fuel hydrocarbons, as indicated in Fig. 5 and 6. Figure 5 shows that the formation of pre-soot hydrocarbons in 0.06 sec at 955°C culminates at an oxygen ratio about 0.05 and then falls off as more oxygen is added. In this experiment, the addition of nitrogen-oxide had a simple effect

on the reaction product as if the mixture of nitrogen and oxygen had been added, as shown in Fig. 6.

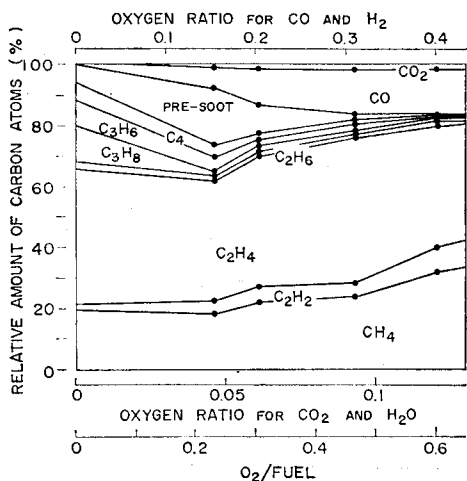


Fig. 5. Relative amount of carbon atoms distributed among the products from mixtures of fuel (37.6%), with nitrogen and oxygen, through the reaction for 0.06 sec at an initial temperature of 955°C.

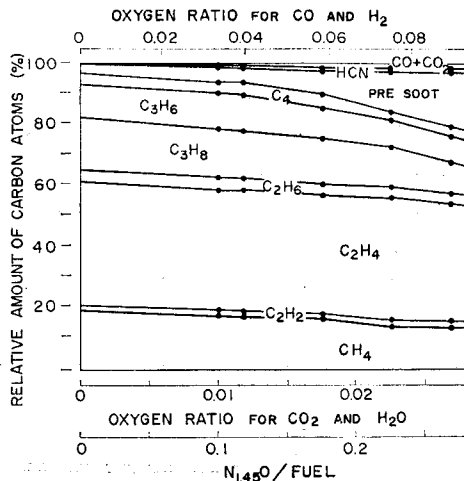


Fig. 6. Relative amount of carbon atoms distributed among the products from mixtures of fuel (46.2%), with nitrogen and nitrogen oxide, through the reaction for 0.06 sec at an initial temperature of 955°C.

Discussion

In an aliphatic fuel flame, the soot particles are assumed to form by decomposition of the fuel to fragment hydrocarbons, followed by the polymerization of the fragment hydrocarbons to polycyclic aromatic hydrocarbons. These polycyclic hydrocarbons, i.e. pre-soot hydrocarbons, are molecules or radicals, and can become soot particles by further polymerization and condensation. If we express the ratio of the mass of carbon atoms distributed among the fuel, the fragment hydrocarbons, and the pre-soot hydrocarbons by $x:y:z$, their rate of change may be simply formulated by a set of differential equations,

$$\begin{aligned} dx/dt &= -k_1(x - K_1 y) \\ dy/dt &= k_1(x - K_1 y) - k_2(y - K_2 z) \\ dz/dt &= k_2(y - K_2 z), \end{aligned}$$

where k_1 and k_2 are reaction rate constants for the decomposition and polymerization reactions, K_1 and K_2 are equilibrium constants between the fuel and the fragment hydrocarbons, and between the fragment and the pre-soot hydrocarbons, respectively, and t is the reaction time.

The solution of the set of equations for appropriate values of k_1 , k_2 , K_1 and K_2 agrees so closely with experimental results that one can estimate the values of k_1 etc. by comparing the experimental results with the solution of the equation. Some examples of fitting of computed curves to the experimental results are given in Fig. 7 to 9.

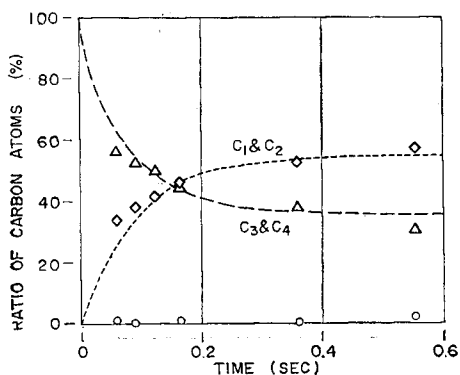


Fig. 7. Fitting of solution of the set of equations to experimentally obtained ratios of carbon atom distributed among fuel and fragment hydrocarbons, starting from a mixture of fuel (37.6%), nitrogen (50.8%), and oxygen (11.6%), through the reaction at an initial temperature of 840°C, assuming $k_1=7$, $k_2=0$, and $K_1=0.65$.

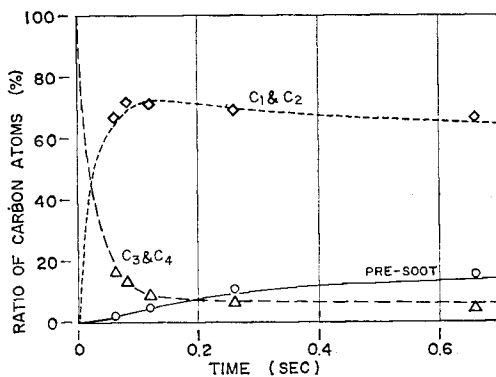


Fig. 8. Fitting of solution of the set of equations to experimentally obtained ratios of carbon atoms distributed among fuel, fragment and pre-soot hydrocarbons, starting from a mixture of fuel (37.6%), nitrogen (44.9%), and oxygen (17.5%), through the reaction at an initial temperature of 905°C, assuming $k_1=28$, $k_2=0.7$, $K_1=0.1$ and $K_2=4.0$.

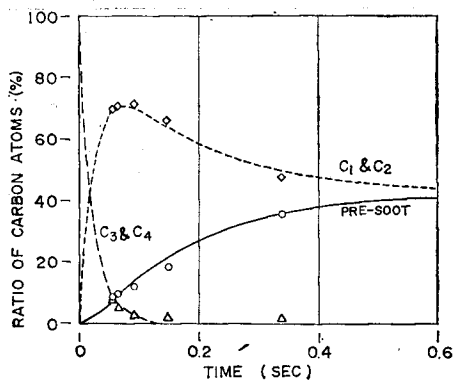


Fig. 9. Fitting of solution of the set of equations to experimentally obtained ratios of carbon atoms distributed among fuel, fragment and pre-soot hydrocarbons, starting from a mixture of fuel (37.6%), nitrogen (50.8%), and oxygen (11.6%), through the reaction at an initial temperature of 955°C, assuming $k_1=40$, $k_2=2.9$, $K_1=0$ and $K_2=1.0$.

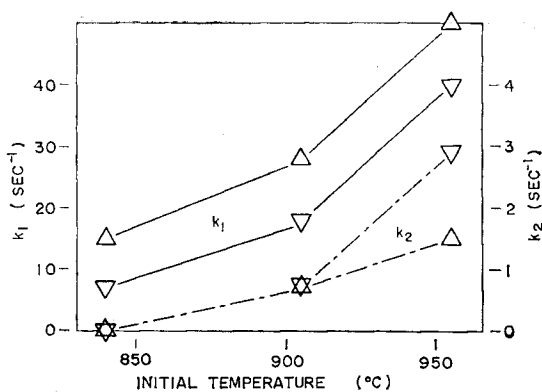


Fig. 10. Rate constants of the decomposition reaction, k_1 , and the polymerization reaction, k_2 , at various initial temperatures for the mixtures of fuel (37.6%) with nitrogen (50.8%) and oxygen (11.6%) (∇), and with nitrogen and oxygen (17.5%) (Δ).

Thus the obtained reaction rate constants k_1 and k_2 are plotted against the initial temperature in Fig. 10. They increase with an increase in the initial temperature, and both are more or less affected by the oxygen ratio. The rate constants at an initial temperature of 955°C are plotted as functions of the oxygen ratio, in Fig. 11. For the decomposition reaction of the fuel hydrocarbons, the rate constant, k_1 , increases monotonically with the addition of oxygen within the range of the experiment. The rate constant, k_2 , of the polymerization reaction to form pre-soot hydrocarbons at an initial temperature of 955°C increases with the addition of oxygen to a maximum value at an oxygen ratio about 0.05 and then decreases. The equilibrium constants k_1 and k_2 decrease with an increase in initial temperature as shown in Fig. 12, and they were little affected by the addition of oxygen within the range of the experiment.

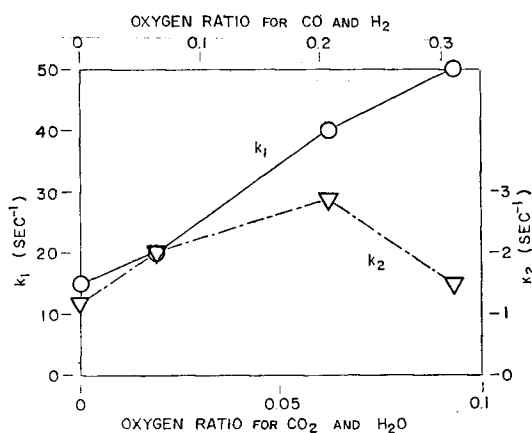


Fig. 11. Rate constants of the decomposition reaction, k_1 , and the polymerization reaction, k_2 , for the mixtures of fuel (37.6%) with nitrogen and oxygen at an initial temperature of 955°C.

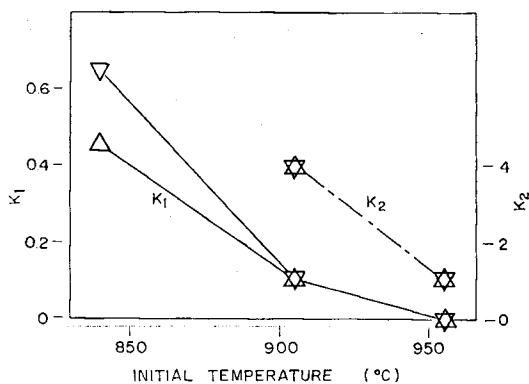


Fig. 12. Equilibrium constants between fuel and fragment hydrocarbons K_1 , and between fragment and pre-soot hydrocarbons, K_2 , at various initial temperatures for the mixtures of fuel (37.6%) with nitrogen (50.8%) and oxygen (11.6%) (Δ), and with nitrogen (44.9%) and oxygen (17.5%) (\triangle).

The major part of the oxygen had been rapidly consumed by combination with hydrogen and carbon at the beginning of the reaction, and it was found as water, carbon-monoxide and carbon-dioxide in quenched product. There were few changes in the amount of these oxides through the reaction time of the experiment. A small percent of the added oxygen remained free in the product during early stages of the experiment, especially at low temperatures, and the free oxygen in the product was found to decrease slowly with reaction time. It has not been found whether the oxides or free oxygen affects the decomposition and polymerization reactions.

Conclusion

Soot-forming reaction at a lower part of diffusion flames is regarded as the sequence of decomposition reaction of fuel hydrocarbons to fragment hydrocarbons, and polymerization reaction of fragment hydrocarbons to pre-soot hydrocarbons which form soot particles by further polymerization and condensation. The decomposition finished virtually within a tenth of a second, but it took a few tenths of a second to reach an equilibrium between the fragment and pre-soot hydrocarbons even at the temperatures above 900°C. The rate of decomposition was linearly accelerated by the addition of oxygen, whereas the rate of polymerization was suppressed by the addition of oxygen beyond an oxygen ratio of about 0.05. This agrees with the fact that a small addition of oxygen or air to the fuel accelerates soot formation in diffusion flames.

The preceding observations¹⁾ indicate that the soot formation begins at about 900°C and is accelerated by addition of a little amount of oxygen or air. Therefore, considerable soot formation occurs at the lower part of a diffusion flame where a little amount of air diffused into the fuel flow and the temperature is about 1000°C.

Nomenclature

- k_1 : reaction rate constant for the decomposition of fuel hydrocarbons into fragment hydrocarbons [sec^{-1}]
- k_2 : reaction rate constant for the polymerization reaction of fragment hydrocarbons to form pre-soot hydrocarbons [sec^{-1}]
- k_1 : equilibrium constant defined as (fuel hydrocarbons)/(fragment hydrocarbons) at an equilibrium
- k_2 : equilibrium constant defined as (fragment hydrocarbons)/(pre-soot hydrocarbons) at an equilibrium
- t : reaction time [sec]
- x : relative quantity of carbon atoms shared by fuel hydrocarbons
- y : relative quantity of carbon atoms shared by fragment hydrocarbons
- z : relative quantity of carbon atoms shared by pre-soot hydrocarbons

Acknowledgment

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