

CHEMICAL KINETIC CHARACTERIZATION OF MODEL FUELS USED FOR DESCRIBING COMBUSTION OF DIESEL

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INTRODUCTION

Recent environmental legislations require the automotive industry to significantly reduce emissions from engines burning diesel. Diesel comprises several aliphatic and aromatic compounds and its exact content varies between different refineries and countries. Several laboratories are currently conducting experiments on test engines to characterize their performance and to determine the influence of various parameters on the rates of pollutants formed. The results will clearly depend on the fuel used in these studies. It is useful to develop model fuels of known chemical composition which can reproduce the physical and chemical characteristics of diesel. These model fuels can then be used in test engines as well as in numerical simulations of engine performance and rates of pollutant formation.

To develop model fuels for diesel, experiments were conducted on a simple and well-known geometry, a laminar non-premixed flame in a counterflow configuration. Although a diesel engine uses turbulent spray combustion at high pressures, the flame on the surface of a tiny droplet can be considered as a laminar non-premixed flamelet [1].

EXPERIMENT

An apparatus, as described in [2],[3] or [4], is used to produce the counterflow flame at atmospheric pressure shown in Figure 1. An oxidizer stream, consisting of air and nitrogen, is directed towards a pool of liquid fuel. A flat thin flame is established between the upper duct and the liquid pool. The heat transferred from the flame to the surface of the pool vaporizes the liquid.

For each oxygen concentration in the oxidizer

stream, a certain strain rate can be found to extinguish the flame. The strain rate is directly proportional to the total oxidizer flow:: $a = 2V/l$ (1)

V is the velocity of the oxidizer stream at the duct exit, l the separation distance between the oxidizer duct and the liquid pool surface. Figure 2 shows the oxygen concentration vs. the strain rate, and gives a first characterization of the reactivity of diverse fuels.

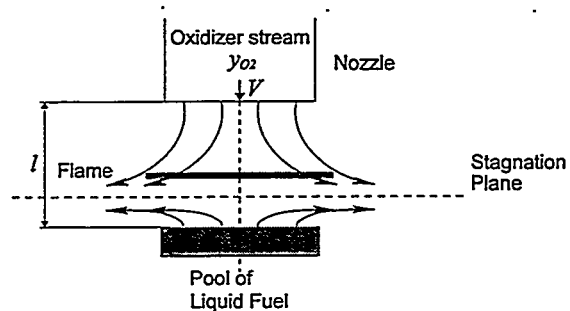


Fig. 1: Schematic illustration of liquid fuel counterflow diffusion flame.

THEORETICAL FORMULATION OF EXTINCTION

One of the first to analyze the structure of a non-premixed flame in a stagnation-point flow was Fendell [5]. Assuming incompressible and inviscid flow, he used a numerical integration to plot the maximum temperature as a function of the Damköhler number, and achieved the characteristic S-shaped curve; its corners identifying the critical conditions of extinction and ignition. For the limit of large activation-energies, Linan [6] achieved analytical results for extinction and ignition conditions for a nonpremixed flame in an inviscid counterflow configuration of two gaseous streams. Krishnamurty et al. [7] extended this analysis to predict extinction of a non-premixed flame

Extinction Data of Hydrocarbon Fuels

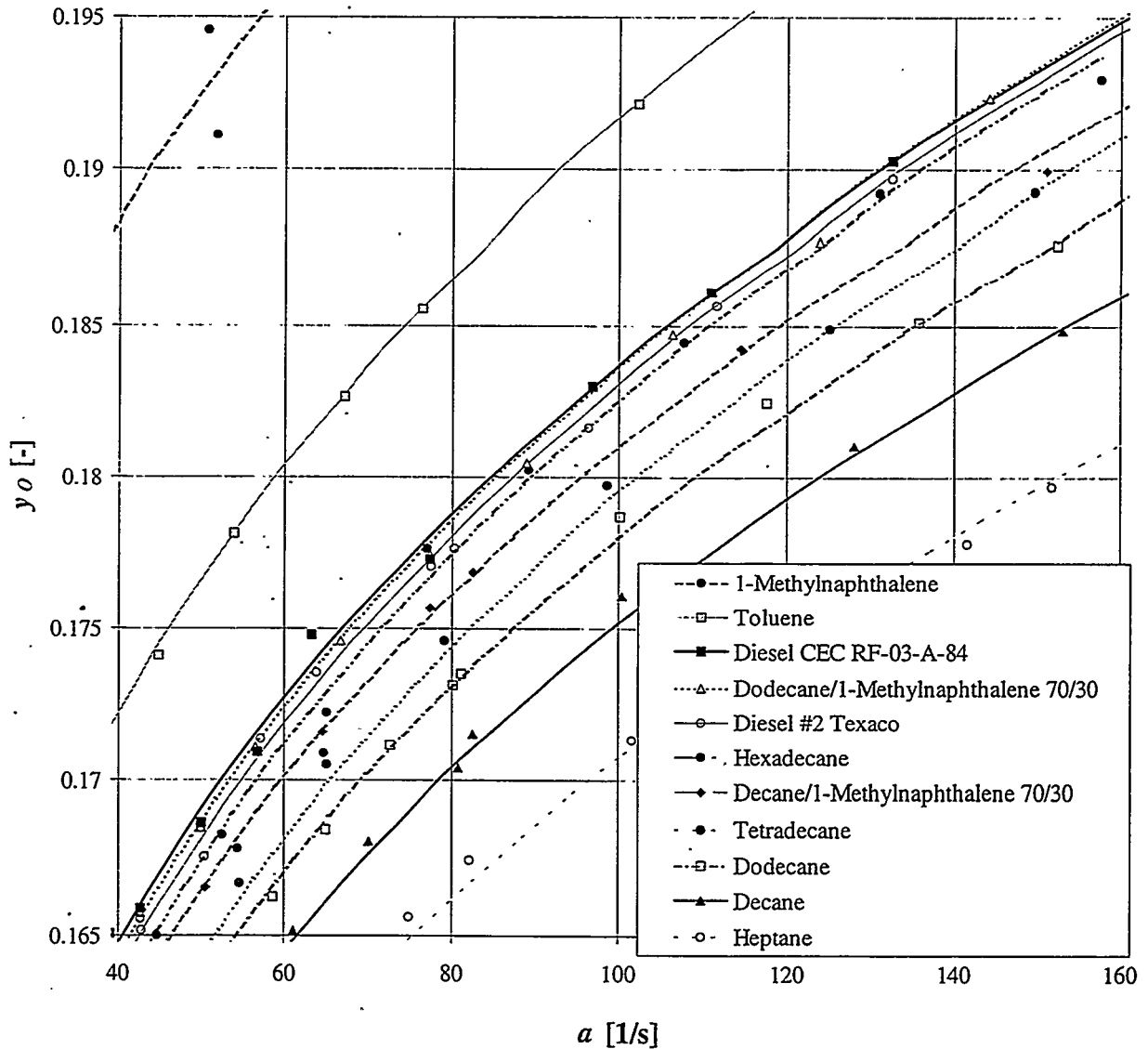


Fig. 2: Extinction data for hydrocarbon fuels.

in the stagnation point boundary layer of a condensed fuel.

Basis for calculation of kinetic parameters from extinction criteria is a one-step overall reaction



ν_o being the stoichiometric molar ratio of oxygen to fuel. Further approximations are that the Lewis numbers for fuel and oxidizer in the gas are unity, that the Prandtl number is constant, and that the product $\mu\rho = \text{constant}$

($\mu = \text{coefficient of viscosity}$, $\rho = \text{density}$).

The Damköhler number is defined as a diffusion time divided by a chemical reaction time and given by [7]

$$D = \rho B_o / [M_F k (du/dr)] \quad (3)$$

where B_o is the pre-exponential factor of consumption of oxidizer, M_F the molecular weight of fuel vapor, and (du/dr) the stagnation point velocity gradient, which is for rotational flow [8]:

$$(du/dr) = V/l. \quad (4)$$

The geometry factor k is 1 for a two-dimensional and 2 for the present axisymmetric flow.

Using the extinction criteria found by Linan [6] and adopted by Krishnamurty et al. [7], and assuming extinction occurring in the diffusion flame regime, the Damköhler number at extinction is given by:

$$D_E = F \cdot \left(\frac{E}{R \cdot T_f} \right)^3 \cdot \exp \left(\frac{E}{R \cdot T_f} \right). \quad (5)$$

E is the activation energy for the reaction (2), and R the universal gas constant. The factor F is a correction factor taking into account the viscous flow in the stagnation-point boundary layer. It can be found as result of a parametric study in Krishnamurty et al. [7], F being a function of T_f , T_∞ , $y_{f,stoich}$ and the fuel properties. T_f is the adiabatic flame temperature calculated by the oxygen and nitrogen concentration of the oxidizer stream and the corresponding stoichiometric fuel

concentration $y_{f,stoich}$. For this theoretical flame temperature it is assumed, that the products are only carbon dioxide and water. T_∞ is the temperature of the oxidizer stream.

Combining the two expressions for the Damköhler number and using the assumptions $\rho B_o = \rho_f B_{of}$ and $\rho_\infty T_\infty = \rho_f T_f$ (ideal gas), one single equation can be formulated describing the extinction condition:

$$\underbrace{\ln \left(\frac{F \cdot a}{\rho_\infty \cdot T_f^2} \right)}_Y = \underbrace{\ln \left(\frac{B_{of} \cdot T_\infty \cdot R^3}{M_F \cdot E^3} \right)}_A - \underbrace{\frac{E}{R}}_B \cdot \underbrace{\frac{1}{T_f}}_X \quad (6)$$

All experimentally measured variables enter through X and Y . A plot of Y over X yields an Arrhenius-plot, where a linear least-square fit can be determined. Its intercept and slope are the parameters A and B , from which B_{of} , and E can be found. Expressing the pre-exponential factor for the molar consumption of fuel:

$$B_F = B_{of} N_o \quad (7)$$

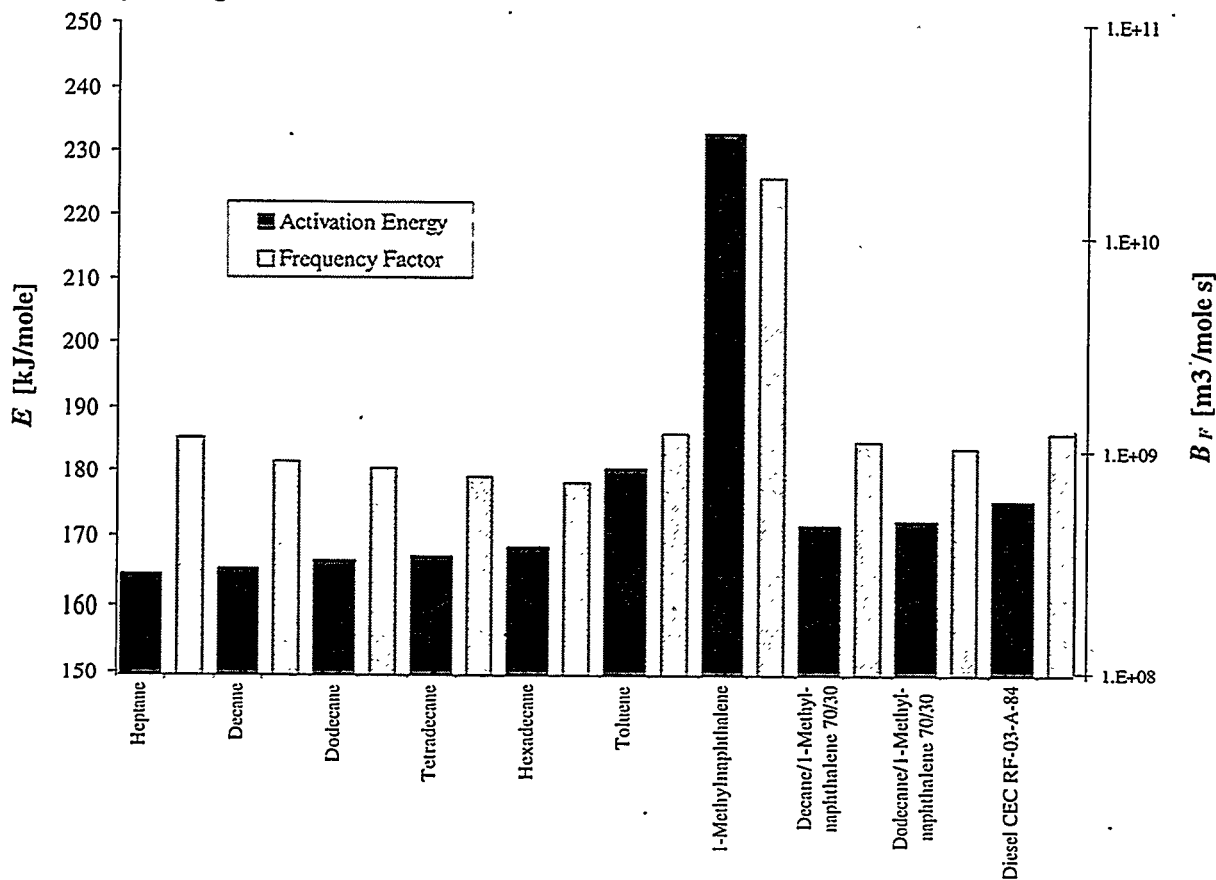


Fig. 3: Activation energies and frequency factors of hydrocarbon fuels

RESULTS AND CONCLUSION

Figure 3 shows the frequency factors and activation energies for the tested fuels. The kinetic parameters for diesel #2 were not calculated due to its unknown composition. The results can be used to describe the molar reaction rate of the fuels:

$$\omega_F = c_F \cdot c_O \cdot B_F \cdot \exp\left(-\frac{E}{R \cdot T}\right). \quad (8)$$

The molar concentrations of fuel and oxidizer, c_F and c_O appear with an exponent of 1 in this equation.

Reviewing the extinction data and activation energies, the mixture dodecane/1-methylnaphthalene (70/30 m%) resembles the results of the CEC-diesel very closely. This was expected, because they have the same amount of aliphatic/aromatic content (70/30). Further study of ignition behavior and pollutant formation is planned, to confirm the proposed fuel as a model fuel for diesel. In this case it is intended to generate a detailed chemical-kinetic mechanism.

List of Symbols

| | | |
|--------|---------------------------|--|
| a | [1/s] | strain rate |
| A, B | [-, K] | constants |
| B_F | [m ³ /kmole s] | pre-exponential rate factor for molar fuel consumption |
| B_O | [m ³ /kmole s] | pre-exponential rate factor for molar oxidizer consumption |
| c | [kmole/m ³] | molar concentration |
| D | [-] | Damköhler number. |
| E | [J/kmole] | activation energy |
| F | [-] | flow factor relating kinetic parameters to extinction conditions |
| k | [-] | geometry factor (1, two-dimensional; 2, axisymmetric) |
| l | [m] | distance between oxidizer duct and fuel surface |
| M | [kg/kmole] | molecular weight |
| r | [m] | radial direction |
| R | [J/kmole K] | universal gas constant |
| T | [K] | temperature |
| u | [m/s] | velocity in radial (r -) direction |
| V | [m/s] | axial velocity at exit of oxidizer duct. |
| X, Y | [1/K, -] | diagram coordinates |

Greek

| | | |
|----------|--------------------------|--|
| μ | [kg/ms] | coefficient of viscosity |
| ν_o | [-] | stoichiometric ratio of oxygen to fuel |
| ρ | [kg/m ³] | density |
| ω | [kmole/m ³ s] | molar reaction rate |

Subscripts

| | |
|----------|-----------------------------|
| E | extinction |
| ∞ | oxidizer stream |
| F | fuel |
| f | equilibrium diffusion flame |
| O | oxidizer |

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