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THERMODYNAMIC MODELING OF THE AUTOIGNITION TEMPERATURE

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Abstract. *The autoignition temperature of 6 fuels was modeled employing lost work analysis. The analysis was performed by dividing an adiabatic premixed flame into two slices, a hot and a cold temperature slice, with an intermediate ignition surface, adopted as reference, and where a single step and complete irreversible chemical reaction occurred. The model employed, an adaptation of the"hot brick problem", assumed that the chemical work and the heat transferred, available at the ignition surface, were fed back to the two slices, initially in thermal equilibrium at the ignition temperature, so that their temperatures departed from the ignition temperature. The lost work obtained was extremized by forming a Lagrangean with an equality constraint due to the adiabatic condition imposed. The stationary lost work was found to be a maximum. The reference surface's temperature (where the chemical reaction occurred) was thus found. The results simulate well the autoignition temperatures of methane, ethanol, ethane and propane, but do not seem to validate the autoignition temperatures of hydrogen and carbon monoxide, which seem to require further model refinement.*

Keywords: *Modeling, Optimization, Autoignition Temperature, Lost Work.*

1. INTRODUCTION

Flammable materials are operated in the process industry and for safety reasons, the knowledge of the autoignition temperature (AIT) of materials is important. Due to the diversity of the materials and due to the frequent occurrence of new materials, together with the experimental limitations, the development of analytical procedures for the reliable determination of the AIT is necessary. AIT is defined as"the lowest temperature at which the substance will produce hot flame ignition in air at atmospheric temperature without the aid of an external ignition source such as a spark or flame" ASTM (2000). Whilst many studies report the use of the molecular characteristics to determine the AIT (e.g. Fang-Yi *et al.* (2012)), in this study we use thermodynamics (lost work).

Lost work analysis employ the combined use of the First and Second Laws of Thermodynamics in order to quantify the irreversibilities involved in a process. When performing work lost analysis, a reference temperature (T_R) must be chosen. The lost work (W_{lost}) is calculated according to eq. 1.

$$Wlost = T_R Sgen \tag{1}$$

Where S_{gen} is the entropy produced within the system.

2. METHODS

The model employed to perform the analysis is an adaptation of the hot brick problem.

In this model, two finite reservoirs at distinct temperatures are available and one wishes to extract the maximum work from them. To achieve this objective, a reversible thermal engine is placed in between the two reservoirs. As heat is exchanged between the hot source and the engine, the temperature of the hot source diminishes. At the same time, heat is exchanged between the engine and the heat sink, raising its temperature. When the hot and cold reservoir reach thermal equilibrium, the engine has produced maximum power (fig. 1)

The adapted problem is one in which there are two subsystems: the interface, where the irreversible chemical reaction occurs, and the reservoirs, or slices, which behave as an inverted version of the hot brick problem (see figs. 2, 3 and 4).

2.1 The reference state

In order to determine the work lost within the system, one has to define a reference state, whose choice is to a degree arbitrary. The flame in study does not interact with the environment, therefore, there is no use in choosing an external

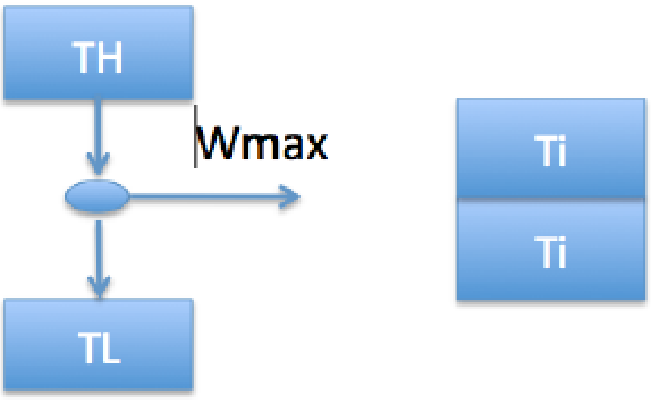

Figure 1. The hot brick problem

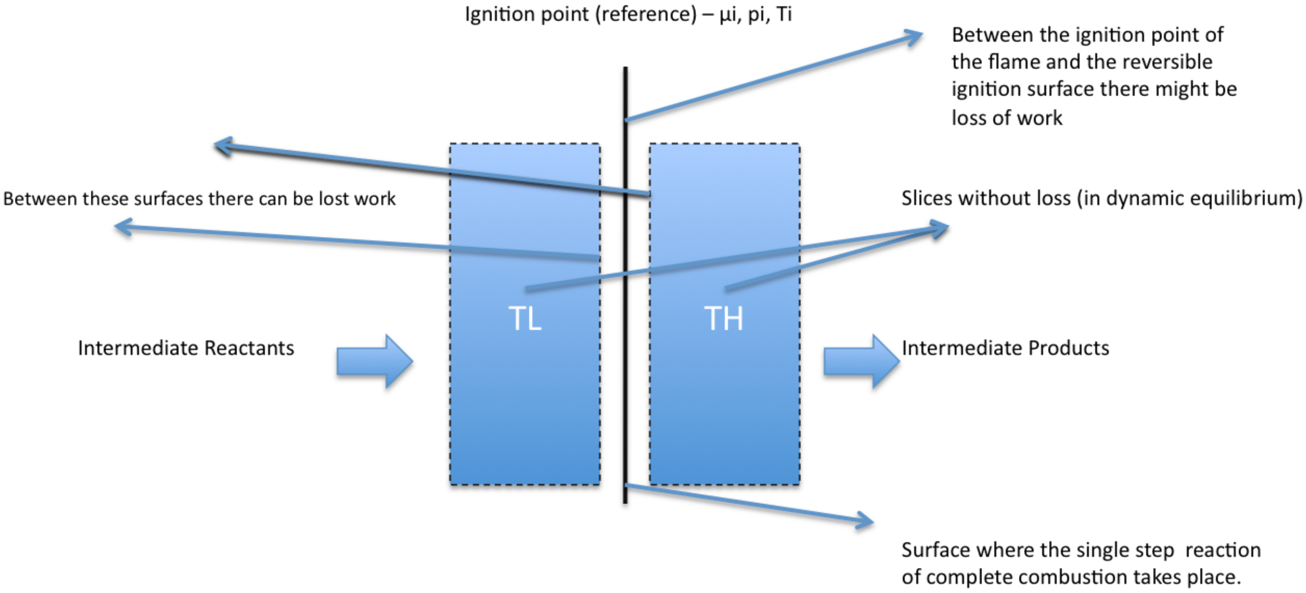

Figure 2. The two slice flme

reference state (this would provide us information solely on the global transformation, giving us no detail of the processes occurring within the flame). One has therefore, to choose an internal reference state.

The choice of the "discontinuity" as a reference allows one, when determining the necessary conditions for stationarity of the lost work, to eliminate the existing two degrees of freedom and determine the state of the "discontinuity". At the "discontinuity", one shall suppose that an instantaneous irreversible reaction of complete combustion occurs.

2.2 Breaking the system into subsystems

One shall break down the flame into two finite thermal reservoirs, separated by a "discontinuity" where an single step complete combustion reaction occurs (chemical reservoir).

Figure 3 shows the subsystem Van't Hoff Equilibrium Box, where the subsystem performs work at as rate equal to $-\Delta\dot{G}^0_R$ on the reservoirs due to a reversible reaction at T_R $(reactants \rightarrow products$, both at the standard state at $T_R)$. The rate of heat exchange due to the reversible reaction is equal to $\dot{Q}_R = T_R \times \Delta\dot{S}^0_R$. This heat is exchanged with the reservoirs (the flame is overall adiabatic).

Figure 4 shows the rate of heat exchange between the interface and the reservoirs, $-\dot{Q}_R$. Chemical work produced at the interface, $-\Delta\dot{G}^0_R$, is partially reinjected to the reservoirs whose temperatures depart from the thermal equilibrium condition (temperature varies from T_R a T_L and from T_R to T_H). The reservoirs simulate an inverted hot brick problem.

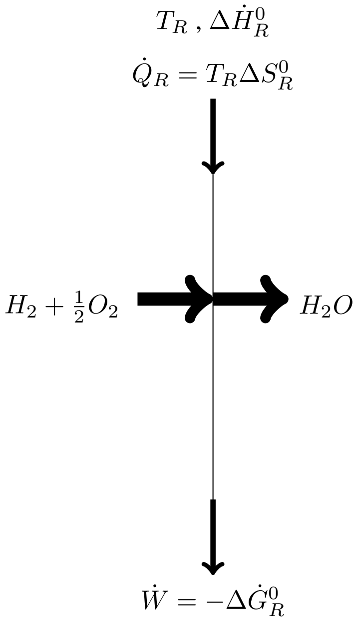

Figure 3. Diagram showing the interface, or infinitesimal Van't Hoff Equilibrium Box.

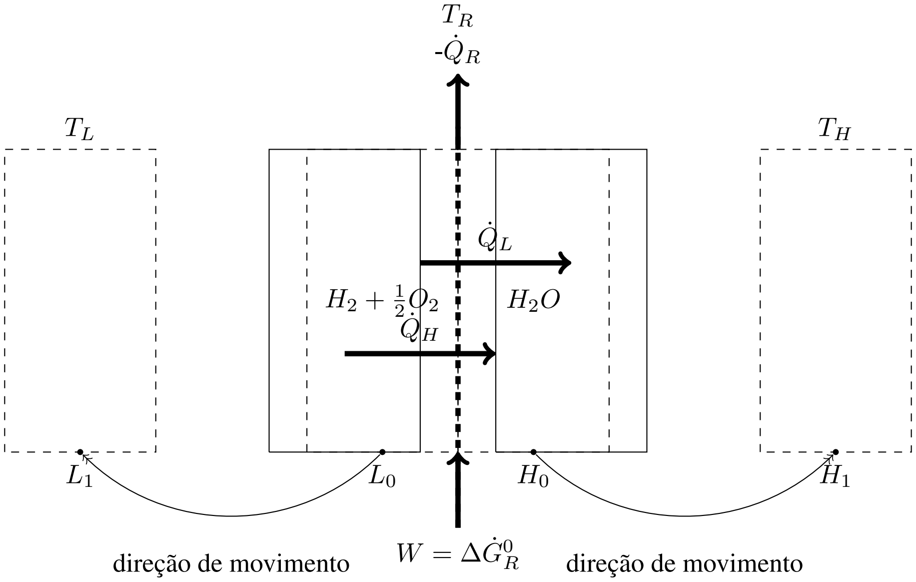

Figure 4. Diagram showing the reservoirs, with their initial and final states (dotted), together with the intermediate state (with $\dot{Q}_L$ and $\dot{Q}_H$).

2.3 MATHEMATICAL PROCEDURE

The mathematical procedure involved generating a Lagrangean of the work lost with the equality constraint as explained above.

For an adiabatic process:

$$\dot{S}_{gen} = \Delta\dot{S}_{system} = \Delta\dot{S}_{interface} + \Delta\dot{S}_{reservoirs} \tag{2}$$

Where, for the interface:

$$\Delta\dot{S}_{interface} = \dot{n}_{H_2}\Delta s^0_R \tag{3}$$

And for the reservoirs:

$$\Delta\dot{S}_{reservoirs} = \dot{n}_{react}\bar{c}_{p_{react}} ln\frac{T_L}{T_R} + \dot{n}_{prod}\bar{c}_{p_{prod}} ln\frac{T_H}{T_R} \tag{4}$$

Where:

$\Delta\dot{S}_{interface}$ is the rate of change of entropy at the interface;
$\Delta\dot{S}_{reservoirs}$ is the rate of change of entropy in the reservoirs;
With the constraint that the loss of enthalpy at the interface equals the enthalpy gain at the reservoirs:

$$\dot{n}_{H_2}\Delta h^0_R + \dot{n}_{react}\bar{c}_{p_{react}}(T_L - T_R) + \dot{n}_{prod}\bar{c}_{p_{prod}}(T_H - T_R) = 0 \tag{5}$$

Thus, one has the Lagrangean, using eqs. 1, 2 and 5

$$L = \dot{W}_{lost} - \lambda(\dot{n}_{react}c_{p_{react}}(T_L - T_R) + \dot{n}_{prod}c_{p_{prod}}(T_H - T_R) + \dot{n}_{H_2}\Delta h^0_R) \tag{6}$$

3. RESULTS

The stationary point of the Lagrangean is obtained by differentiating the Lagrangean of the irreversible flame relative to its variables (λ, T_R e T_H; T_L was considered 298K) and equating these equations to zero. One obtains the extremum by solving the three equations 7, 8 and 9 simultaneously:

$$\frac{\partial L}{\partial T_R} = \Delta\dot{S}^0_R + \dot{n}_{react}\bar{c}_{p_{react}} ln\frac{T_L}{T_R} + \dot{n}_{prod}\bar{c}_{p_{prod}} ln\frac{T_H}{T_R} - (\dot{n}_{react}\bar{c}_p + \dot{n}_{prod}\bar{c}_p)\lambda = 0 \tag{7}$$

$$\frac{\partial L}{\partial T_H} = \dot{n}_{prod}\frac{\bar{c}_{p_{prod}}T_R}{T_H} - \lambda\dot{n}_{prod}\bar{c}_{p_{prod}} = 0 \tag{8}$$

$$\frac{\partial L}{\partial \lambda} = \dot{n}_{react}\bar{c}_{p_{react}}(T_L - T_R) + \dot{n}_{prod}\bar{c}_{p_{prod}}(T_H - T_R) + \dot{n}_{H_2}\Delta\ h^0_R = 0 \tag{9}$$

The autoignition temperatures used as comparison came from Association (2014).
The columns $\overline{\dot{n} \times c_p}$ were calculated using the 7 coefficient NASA polynomials Mc Bride and Burcat (1994).

The average considered used temperatures ranging from T_L=298K até T_R for the reactants (fuel plus stoichiometric oxygen) and ranging from T_R to T_H for the products of complete combustion (limited to 6000K, which is the range of validity of the polynomials used).

Δh^0_{comb} e Δs^0_{comb} were calculated at the reference temperature (ignition temperature).

After solving for these equations, one obtains the reference temperature of stationary irreversibility, as shown in table 1.

In order to determine what kind of an extremum is the W_{lost}, one has to calculate the *Bordered Hessian* matrix. It is given below:

$$\begin{bmatrix} 0 & g_1 & g_2 \\ g_1 & L_{11} & L_{12} \\ g_2 & L_{21} & L_{22} \end{bmatrix}$$

Where:

Table 1. Comparison of the reference temperature of stationary irreversibility with the autoignition temperature

Fuel	T_{autoig} K	$T_{ign_{statirrev}}$ K	T_H K	$\overline{\dot{n}_{react}c_{p_{react}}}$ J/K	$\overline{\dot{n}_{prod}c_{p_{prod}}}$ J/K	Δh^0_{comb} kJ/mol	Δs^0_{comb} $J/mol/K$
H_2	833	342	4971	43	52,7	-242	-45,8
CO	878	248	4756	49,8	60,9	-277	-83,8
CH_4	868	759	5705	110	172	-800	0,464
CH_3OH	728	868	5175	113	171	-672	52
C_2H_6	745	859	6137	196	291	-1426	54,3
C_3H_8	723	888	6306	284	408	-2044	105

f = $\dot{W}_{lost}$;
g = $\overline{\dot{n}_{react}c_{p_{react}}}(T_L - T_R) + \overline{\dot{n}_{prod}c_{p_{prod}}}(T_H - T_R) + \dot{n}_{H_2}\Delta h^0_R$;
a = (T_R, T_H);
and the indices represent the variable to which the partial derivative is to be calculated.

The matrix is found to be negative definite. The sufficient condition for this is:

$$\left|H_1^B\right| < 0 \text{ e } \left|H_2^B\right| > 0 \tag{10}$$

Where:

$$\left|H_1^B\right| = \begin{vmatrix} 0 & g_1 \\ g_1 & L_{11} \end{vmatrix} \text{ e } \left|H_2^B\right| = \begin{vmatrix} 0 & g_1 & g_2 \\ g_1 & L_{11} & L_{12} \\ g_2 & L_{21} & L_{22} \end{vmatrix} \tag{11}$$

The determinants were calculated:

$$\left|H_1^B\right| = \begin{vmatrix} 0 & -(c_{p_{react}} + c_{p_{prod}}) \\ -(c_{p_{react}} + c_{p_{prod}}) & L_{11} \end{vmatrix} = -(c_{p_{react}} + c_{p_{prod}})^2 < 0 \tag{12}$$

and:

$$\left|H_2^B\right| = \begin{vmatrix} 0 & -(c_{p_{react}} + c_{p_{prod}}) & c_{p_{prod}} \\ --(c_{p_{react}} + c_{p_{prod}}) & -\frac{c_{p_{reag}}+c_{p_{prod}}}{T_R} & \frac{c_{p_{prod}}}{T_H} \\ c_{p_{prod}} & \frac{c_{p_{prod}}}{T_H} & -\frac{T_R c_{p_{prod}}}{T_H^2} \end{vmatrix} =$$

$$\frac{c_{p_{prod}}(c_{p_{prod}} + c_{p_{reag}})}{T_H^2 T_R}(-2c_{p_{prod}}T_R T_H + c_{p_{prod}}T_H^2 + (c_{p_{prod}} + c_{p_{react}})T_R^2) >$$

$$> \frac{c_{p_{prod}}(c_{p_{prod}} + c_{p_{reag}})}{T_H^2 T_R}(\sqrt{c_{p_{prod}} + c_{p_{reag}}}T_R - \sqrt{c_{p_{prod}}}T_H)^2 > 0 \tag{13}$$

Since the Bordered Hessian was found to be negative definite, the rate of work lost found turned out to be a maximum.

4. DISCUSSION AND CONCLUSIONS

The identification of the reference temperature with the ignition surface temperature, where ignition occurred, was found to allow one to determine the AIT of 4 out of 6 fuels with some degree of precision using thermodynamics alone. A working principle was forwarded. The principle of maximum work lost resembles the Maximum Entropy Production Principle (MEP), but has the advantage of accomodating a calculated reference temperature which is not necessarily that of the environment.

The ignition temperature was considered to be the reference temperature at which maximum internal irreversibility resulted.

The degree of success of the simulation allows one to infer that selected kinetic phenomena might be analysed using thermodynamics.

The adoption of the environmental temperature as reference is merely an *a prioristic* constant of proportionality between the generated entropy and the work lost. It is to be noted in this model, that the entropy generated and the work lost have a distinct status, being the constant of proportionality between them, the reference temperature, calculated by an optimisation procedure.

Whilst the results obtained indicate that the model has a potential to be further developed, it nonetheless indicate, too, that refinements are necessary.

5. ACKNOWLEDGEMENTS

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