DETONATIONS INHIBITION BY HALOCARBONS*

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Halon 1301,a typical chemical inhibitor of flame influences the detonation phenomenon However,the ban of halons production by the Montreal Protocol in 1994 has raised the question to find out substitutes.A comparative study of the respective efficiency of the other halocarbons (CFC,HFC,HCFC) indicates the role of bromine atoms in the inhibition mechanism. Measurements of the detonation structure and velocity are reported for several CO/H2/O2/Ar mixtures with and without halocarbon additives.They will be compared and their actions will be discussed in terms of induction times behind the leading shock by using a ZND model.

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INVESTIGATED BURNING GASEOUS MIXTURES

$H_2/CO/O_2/AR+INHIBITORS$

Inhibitors examined:

Halons :CF_3Br, CF_2HBr
CFC's :CF_3Cl, CF_2Cl_2, $CFCl_3$
HFC's :CF_3H, C_2F_5H, CF_3-CFH_2
HCFC's :CF_2HCl, CF_3-$CFHCl$
FC's :CF_4, C_3F_8

The initial composition of gaseous mixtures is fixed by **4** parameters

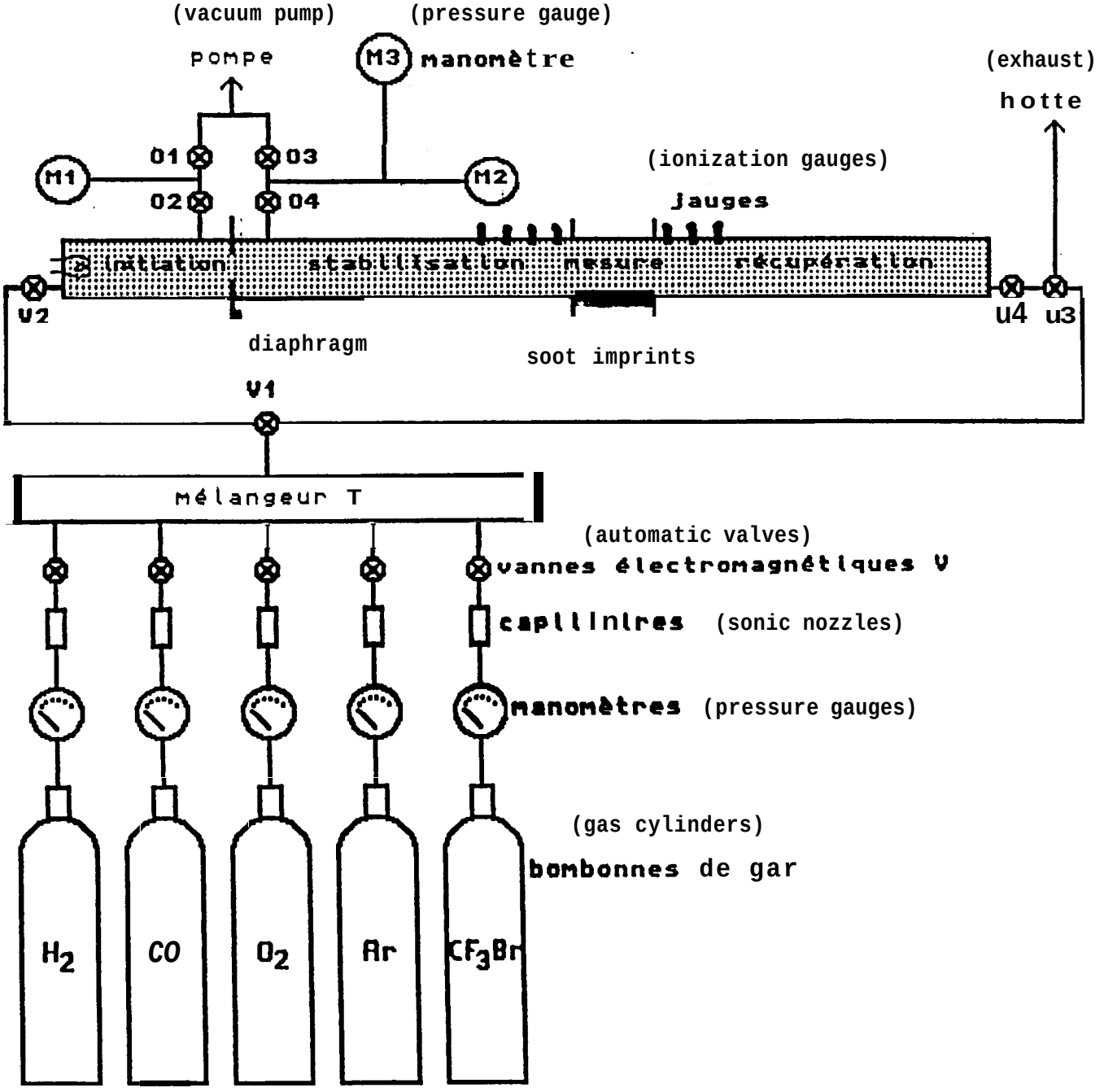
$$\beta = \frac{X_{H_2}}{X_{H_2} + X_{CO}} \qquad 1.00,\ 0.25,\ 0.1,\ .05$$

$$\alpha = X_{Ar} + X_{INH} \qquad 0.5\ ,0.3$$

$$\Phi = \frac{X_{H_2} + X_{CO}}{2X_{O_2}} \qquad 1.00$$

$$X_{INH} \qquad 0, \ldots\ldots 0.10$$

EXPERIMENTAL SETUP OF THE DETONATION TUBE



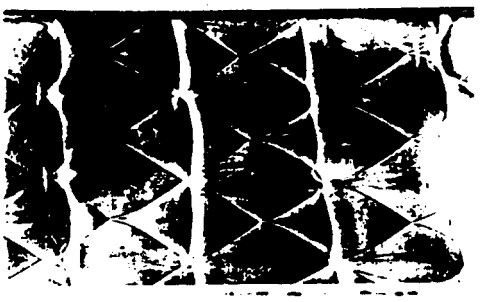
SOOT IMPRINTS OF DETONATION WAVES

variable initial pressure at left
variable CF_3Br amount at right.

P

% CF_3Br

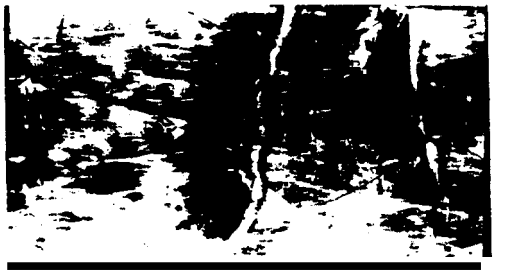
150



0

10 cm

100



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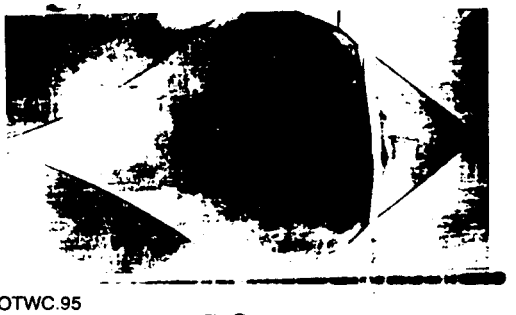
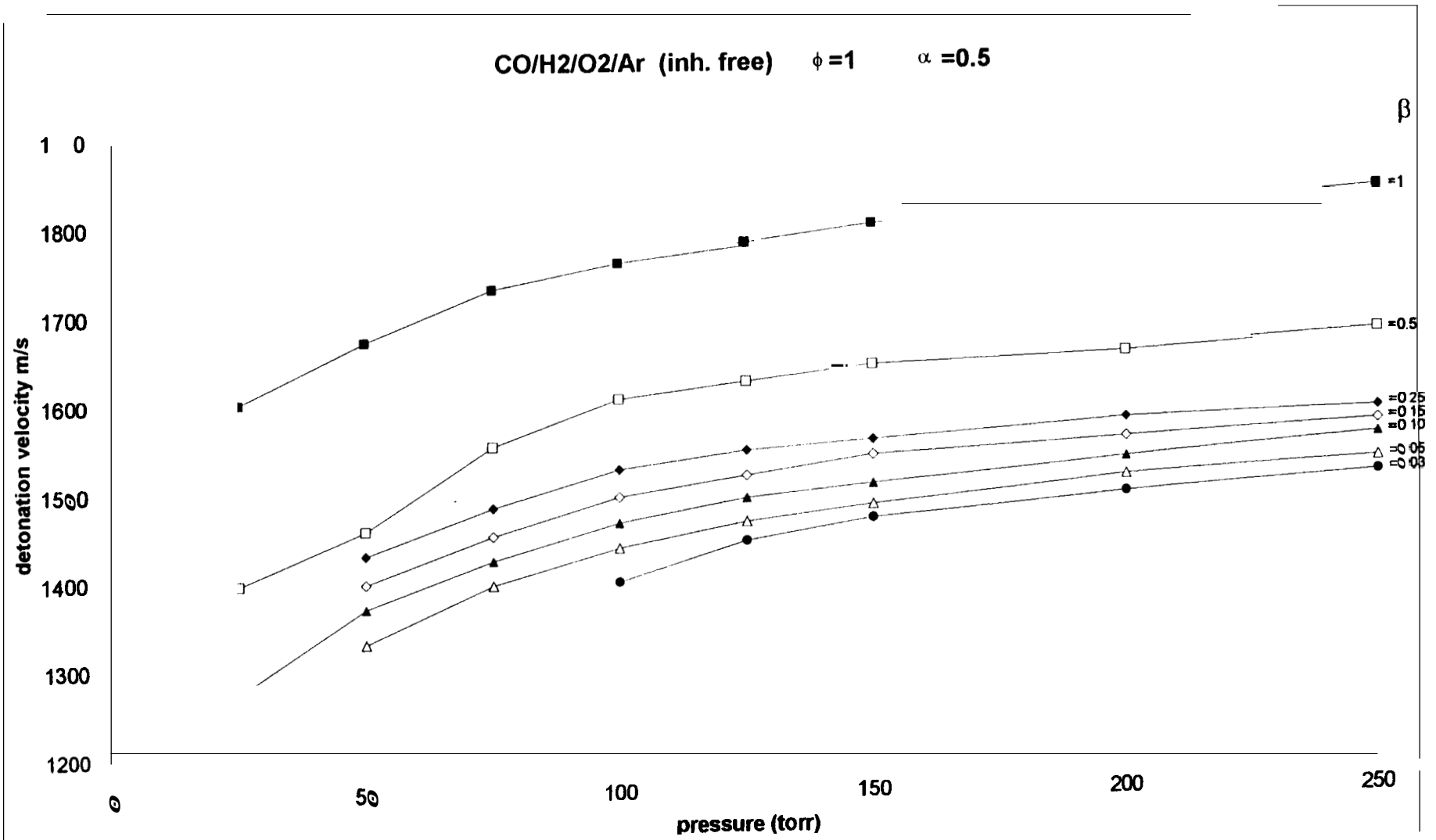
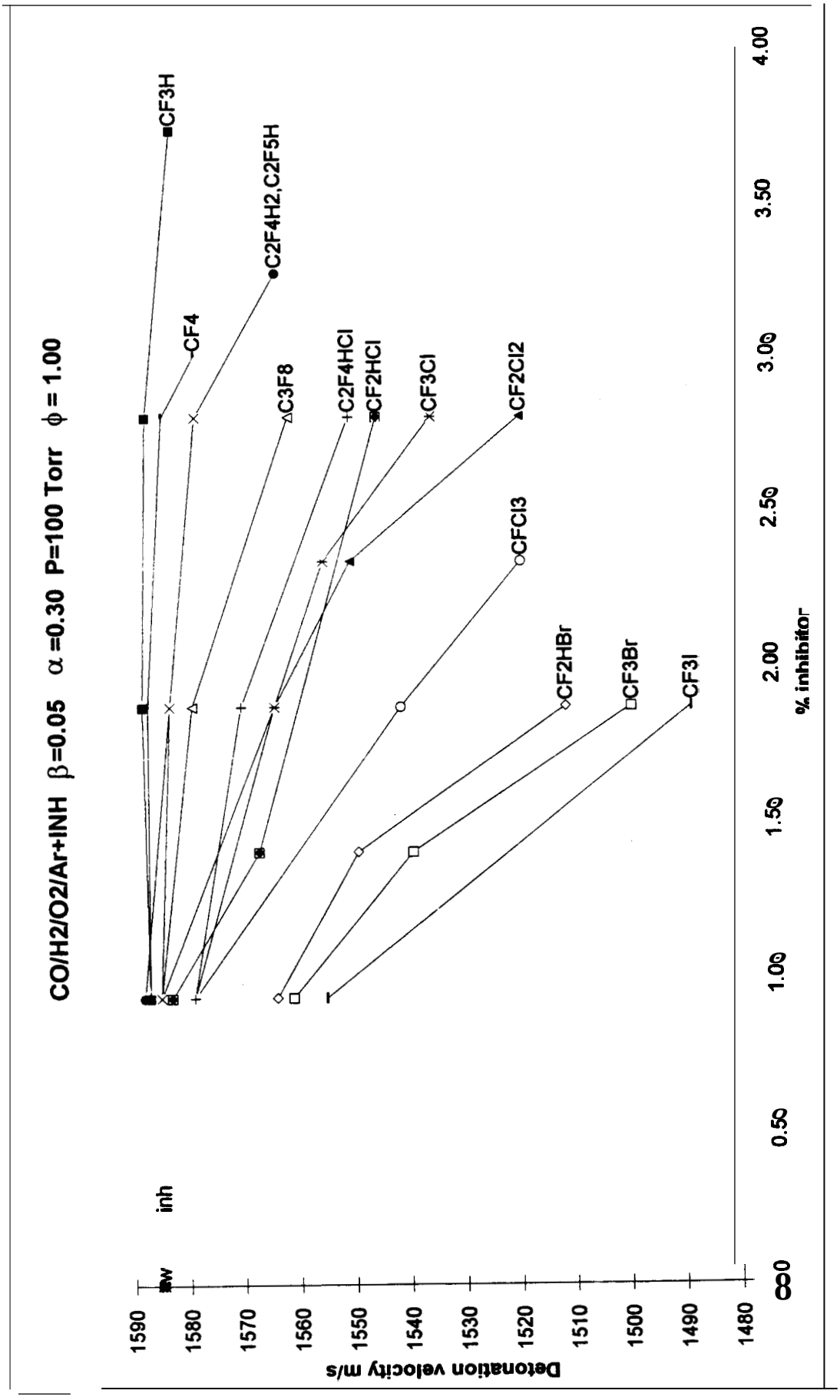


50

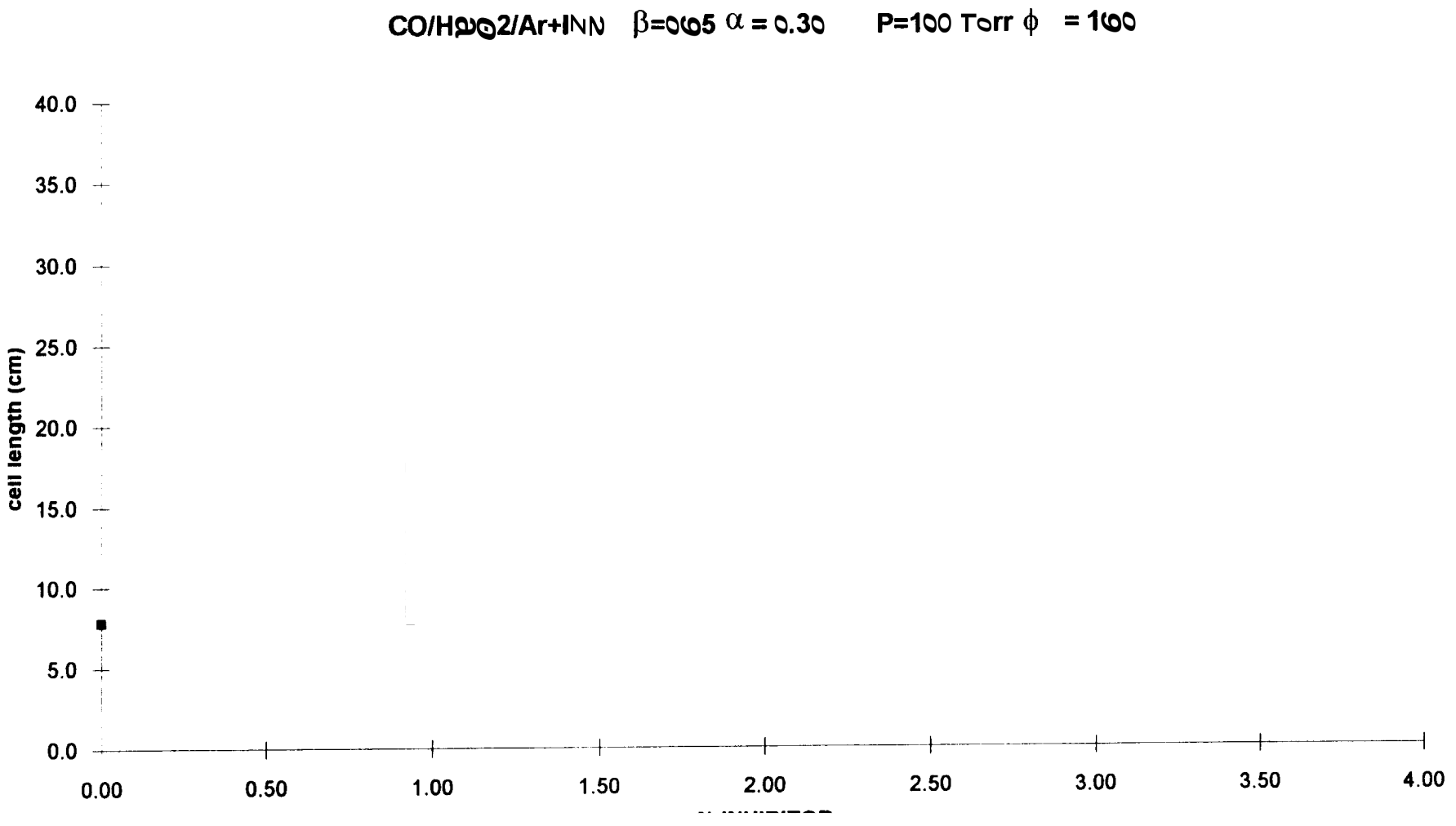
4



DETONATION VELOCITY vs. INITIAL PRESSURE FOR UNINHIBITED MIXTURES WITH VARIABLE H_2 CONTENT



DETONATION VELOCITY vs. PERCENTAGE OF ADDITIVE FOR VARIOUS INHIBITORS



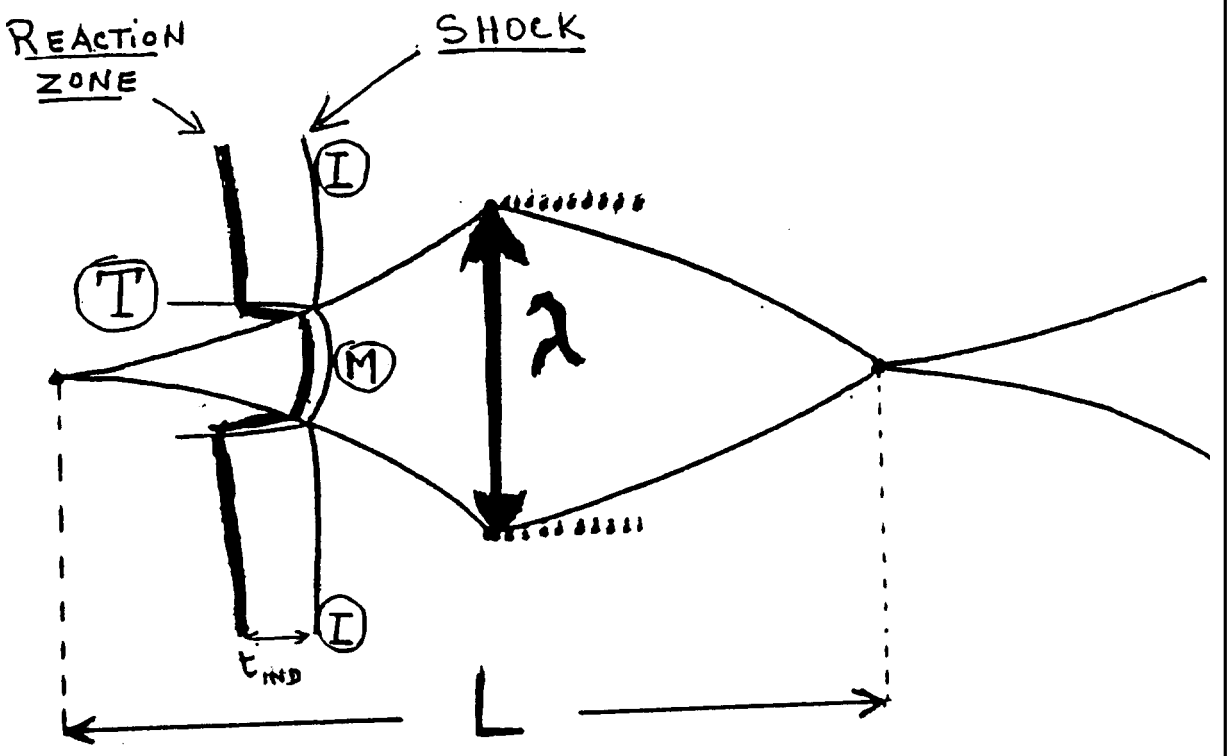
DETONATION CELL LENGTH vs. PERCENTAGE OF ADDITIVE FOR VARIOUS INHIBITORS

SCHEMATIC DIAGRAM OF THE CHARACTERISTIC PARAMETERS OF DETONATION STRUCTURE

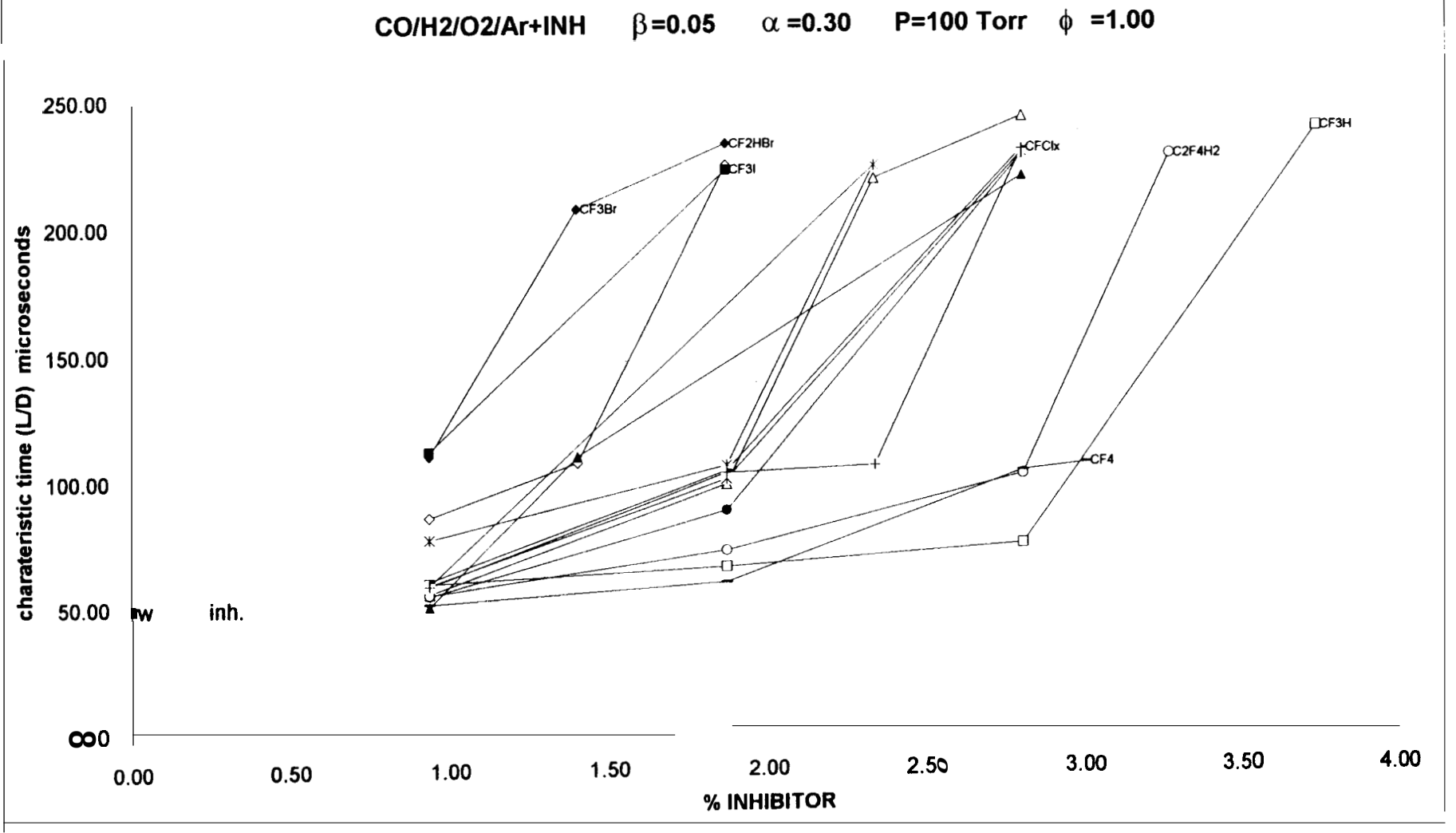
$$t_{CAR} = \frac{L}{D}$$

← CELL LENGTH

← EXP. DETONATION VELOCITY

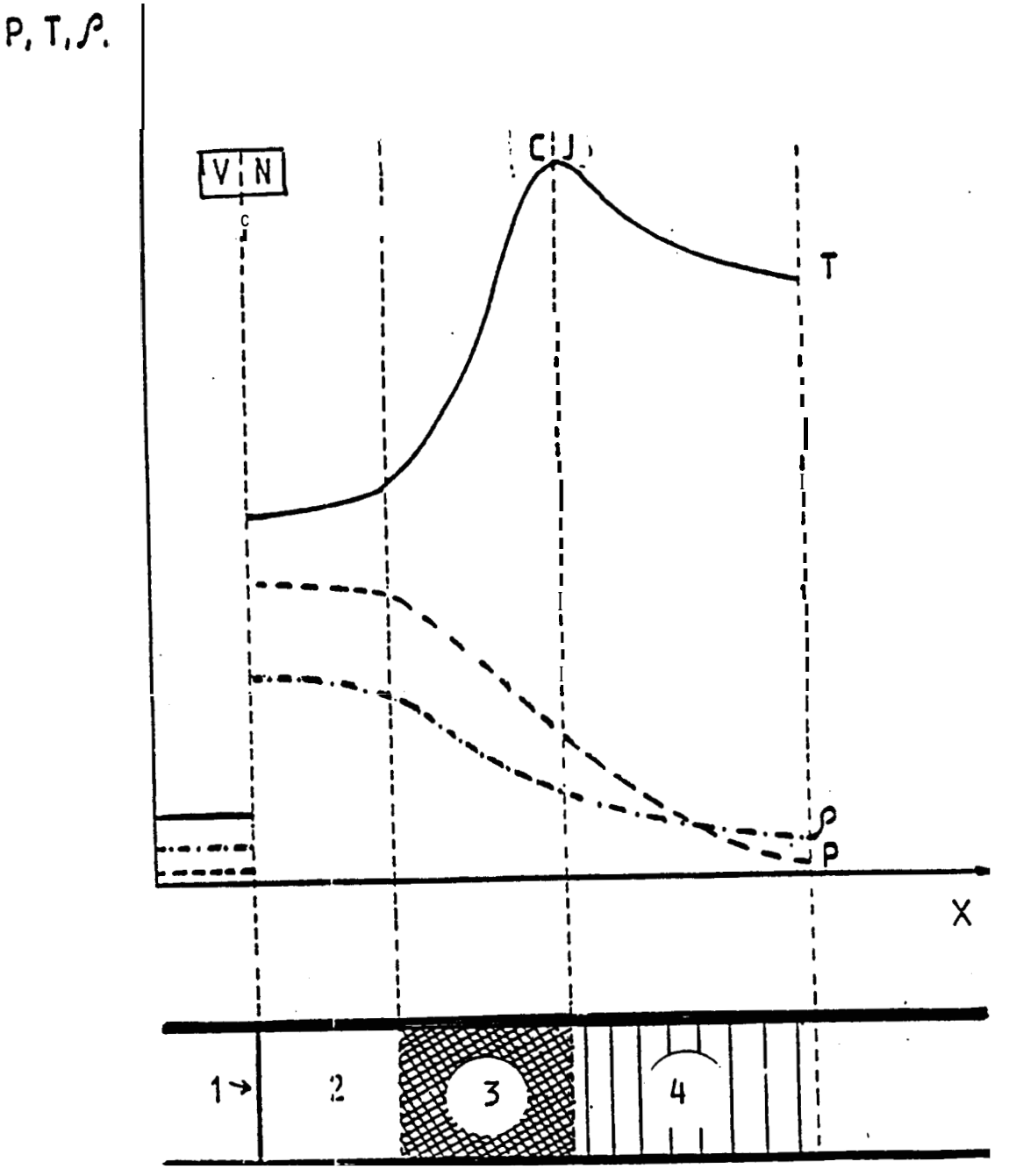


$$t_{CAR} = K_1 \, t_{IND}$$



DETONATION CHARACTERISTIC TIME vs PERCENTAGE OF ADDITIVE FOR VARIOUS INHIBITORS

Z N D MODEL **SCHEMATIC DIAGRAM**



1. Shock Wave
2, Ignition Zone
3. Reaction Zone
4, Expansion Wave

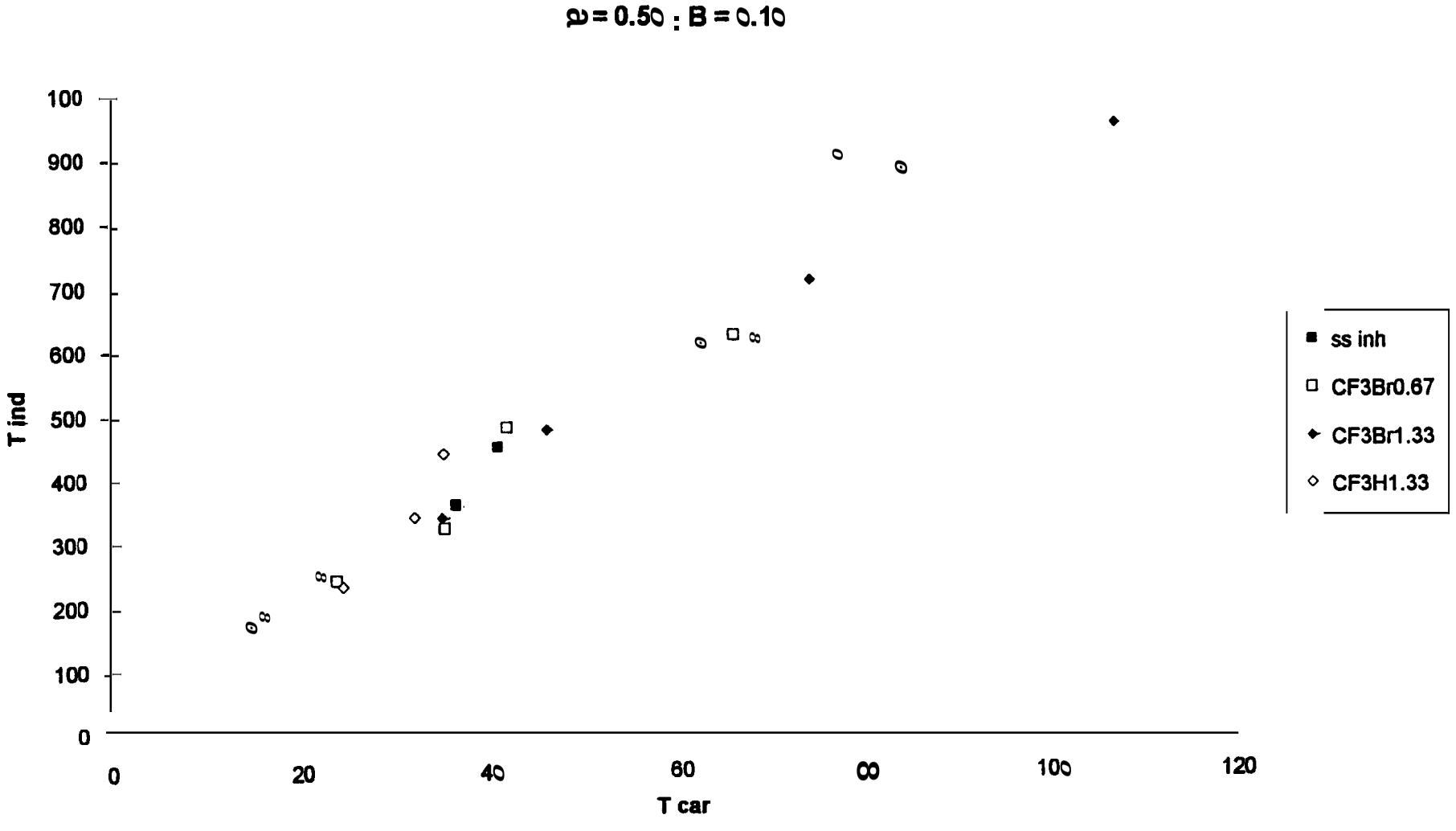
Z N D model **KINETICAL** MECHANISM

It is possible to deduce an induction time from a simplified chemical mechanism

$H_2 + O_2 \rightarrow 2\,0\,H$	
$H + O_2 \rightarrow OH + O$	r.1
$O + H_2 \rightarrow OH + H$	r.2
$OH + H_2 \rightarrow H_2O + H$	r.3
$CO + OH \rightarrow CO_2 + H$	**r.4**
$H \rightarrow$ products	r.5a
inh + OH $\rightarrow$ intermediate	r.5b
O +products + OH	r.5c
$H + O_2 + M \rightarrow HO_2 + M$	r.6

Reaction Mechanism introduced in the ZND model

reaction	A ($l\ mol^{-1}\ s^{-1}$)	n	Activation energy cal/mole
$H_2 + O_2 \rightarrow 2\,0\,H$	$1.00\ 10^8$	0.0	40000
$H + O_2 \rightarrow OH + O$	$2.24\ 10^{11}$	0.0	16800
$O + H_2 \rightarrow OH + H$	$1.74\ 10^{10}$	0.0	9450
$H_2 + OH \rightarrow H_2O + H$	$2.19\ 10^{10}$	0.0	5550
$CO + OH \rightarrow CO_2 + H$	$2.32\ 10^9$	0.0	5700
$H + O_2 + M \rightarrow HO_2 + M$	$1.59\ 10^9$	0.0	-1000
$CF_3Br + H \rightarrow CF_3 + HBr$	$2.20\ 10^{11}$	0.0	9450
$CF_3H + H \rightarrow CF_3 + H_2$	$1.16\ 10^{11}$	0.0	17470
$CF_3H + OH \rightarrow CF3 + H_2O$	$2.65\ 10^1$	2.4	3088
$CF_3H + O \rightarrow CF3 + OH$	$1.10\ 10^9$	0.0	3187
$CF_2HCl + H \rightarrow CF_2H + HCl$	$4.65\ 10^{11}$	0.0	15361
$CF_2HCl + OH \rightarrow CF_2Cl + H_2O$	$1.28\ 10^9$	0.0	3320
$CF_2HCl + O \rightarrow CF_2Cl + OH$	$7.00\ 10^9$	0.0	8584



RELATION BETWEEN COMPUTED INDUCTION TIME AND MEASURED CHARACTERISTIC TIME

CONCLUSIONS

Br and I contaiiiing compounds are the most efficient mhibitors to avoid detonation.

CF_3Br are a little more efficient that CF_2HBr because of the presence of H in this last compound.

The presence of H elements in the fluorocarbon molecule does not influence strongly the inhibition effect.

CF_4 and CF_3H have similar action on the inhibition.

The inhibiting effect of the presence of chlorine elements in the molecule depends on the number of chlorine atoms.

The action of the inhibitor is better when the percentage of H_2 in the total fuel content is small.

The first attack of the fluorocarbon compound by radicals and mainly H atoms is essential. Its rate will depend strongly on the rate coefficient. Furthermore, the subsequent reactions of HX with radicals leading to the formation of X atoms will be important for the inhibition.

Induction time calculations by a simple model give a good approach about the influence of the first attack.
So, CF_3Br, CF_2HBr and CF_3I will react relatively fast with H atoms producing HBr or HI. They interfere with the branching process like a recombination reaction.

The presence of large quantities of F in the molecule acts as a scanvenger of H atoms, but plays only once, HF is a stable compound.

Finally, CF_3I could be an alternative inhibitor for detonation if its ODP is low enough. However, its role must be checked more in details.