Warsaw University of Technology

FACULTY OF
POWER AND AERONAUTICAL ENGINEERING

Institute of Heat Engineering

Half-semester Project

for subject "Computer Methods in Combustion"

Theoretical study of influence on explosiveness of hydrogen-air mixture with various content of nitrogen.

Hubert Demianowski
Michał Forysiak
Aleksander Kipiela

supervisor
dr inż. Mateusz Żbikowski

Warsaw, 2019

Abstract

This paper was written as a half-semester project for “Computer Methods in Combustion”, subject conducted on 6th semester of Aerospace Engineering, specialization Propulsion Systems, in Warsaw University of Technology, faculty of Power and Aeronautical Engineering. Its main purpose was to show students possibilities of Cantera SD toolbox package. Basic calculations of detonation cells parameters are performed.

Keywords: detonation structure, detonation cell, cantera SD toolbox, hydrogen-air mixture detonation

Contents

1 Introduction

1.1 Basic theories

Chapman-Jouquet theory is the most known theory to describe and predict behaviour of gases under circumstances of detonation. Theory models detonation as a propagating shock wave with heat being released at its front. Equations describing it are very simple, yet results obtained are surprisingly similar to measured ones. However, using this theory we cannot predict what happens along shock wave stated above. More complex theory describing it was developed by Zel'dovich, von Neumann, and W. Doering. It is called ZND theory. In this theory, detonation is modelled not as a single schock wave, but as a shock wave followed by zone of exothermic chemical reactions.

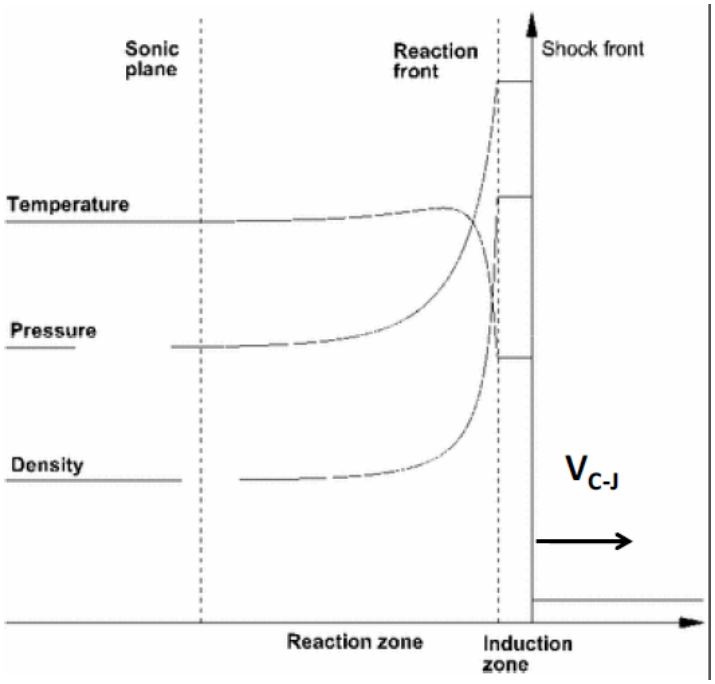

Figure 1: Change of parameters in reaction and induction zones of ZND theory

1.2 Structure of detonation

Both of these theories stated describe detonation as one-dimensional processes, but we know from experiments that it has spatial structure. Thus, both theories can only be used to derive average parameters of detonation, but are unable to predict its behaviour locally. One of methods to observe this spatial structure is using plates covered in soot. When detonation propagates along such a plate, pressure waves leave marks on soot. Structure which can be observed is made of so called detonation cells. Width of this cells is important parameter using which we are able to compare explosiveness of different gaseous mixtures. Such results are key feature when it comes for example to designing systems which are using dangerous gaseous mixtures. One of the most well known databases for such results was set by Explosion Dynamics Laboratory at California Institute of Technology.

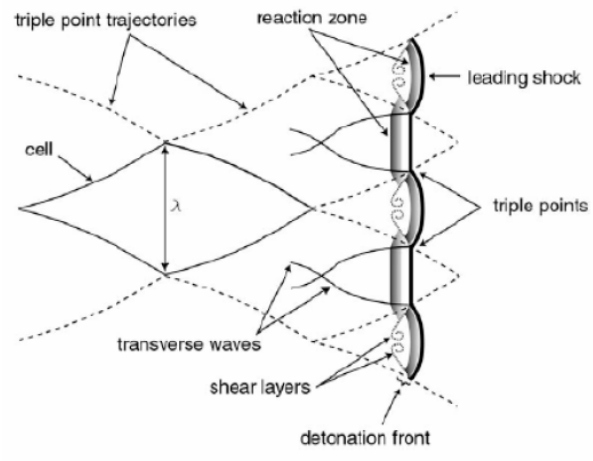

Figure 2: 3D structure of detonation
A picture is showing structure of detonation

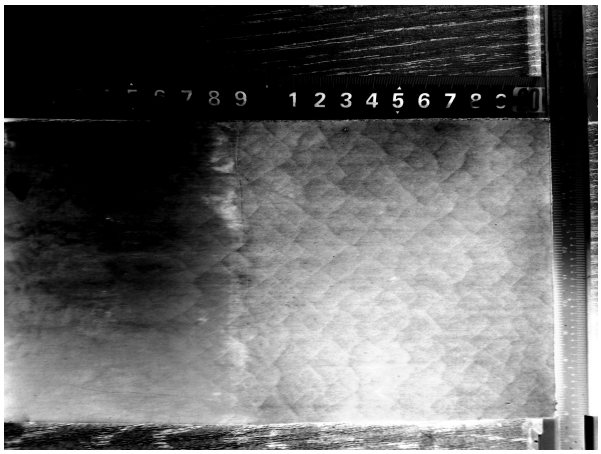

Figure 3: Detonation structure in soot
Photo shows detonation structure visible on plate covered in soot. It was taken during laboratory excerieses at Warsaw Univeristy of technology. This structure was obtained for H2-air mixture with 29,6% of hydrogen

1.3 Aim of project

Hydrogen has been recognized as a promising energy carrier due to its unique advantages, such as high calorific value and reduced NOx / SOx emission. Currently, hydrogen is used widely in industrial process, such as Haber process, transportation and chemical power plants. However, safety problems still persist constantly on account of its wide flammability limit, high explosion pressure and rate of pressure rise.

The possibility of self-ignition hydrogen-air mixture depends on concentration. At a temperature of 293 K, the mixture may ignite spontaneously if the hydrogen concentration is from 4 to 75% by volume. Mixtures with particularly explosive properties are obtained in the range of hydrogen concentration 18 - 65%. The use of hydrogen gas is dangerous due to the flammability and explosiveness of this element and requires special care.

By adding neutral nitrogen to mixture we can reduce the effect of detonation occured due to failure of hydrogen container or leakage in any system. Aim of this project is to check, using SD Toolbox for Cantera, size of detonation cell using various correlations (Gavrikov, Westbrook, Ng et al), for various volume content of nitrogen in hydrogen-air mixture.

2 Model Description

Calculations were based on ZND and CV models of detonation with the shock front traveling at the CJ speed. Through evaluating various measures of the reaction zone thickness and exothermic pulse width, effective activation energy and Ng stability parameter, estimations of the cell size were obtained. Detonation cell width was estimated with three correlations: Gavrikov's, from Ng, Hoi Dick, Yiguang Ju, and John H. S. Lee and Westbrook's.

3 Results

As a result of calculations, following plots were obtained:

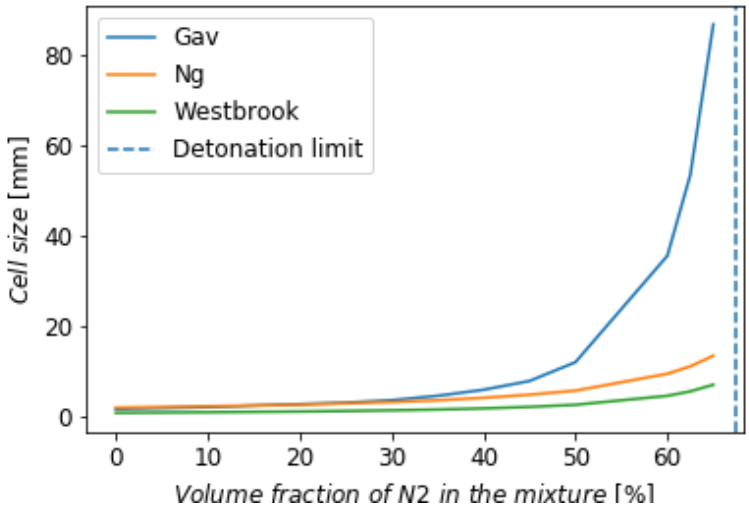

Figure 4: Cell size
Gavrikov, Ng et al and Westbrook correlation on one graph. One can notice, that Gavrikov's correlation gives much higher values of detonation cell size for high fraction of N2 in mixture. They may be more realistic, because Gavrikov's correlation was tested numerically.

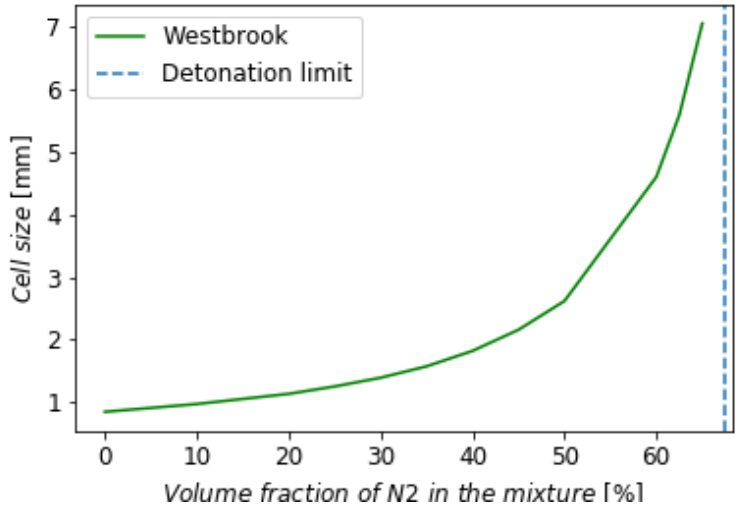

Figure 5: Cell size Westbrook
For Westbrook correlation one can read, that cell size for higher volume fraction of nitrogen is still comparatively low and the mixture is dangerous.

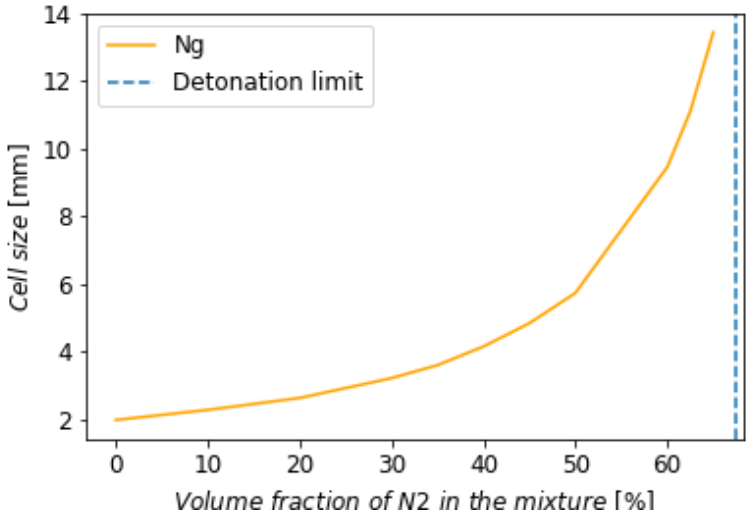

Figure 6: Cell size Ng
For Ng et al correlation the conclusions are similar to those for Westbrook correlation

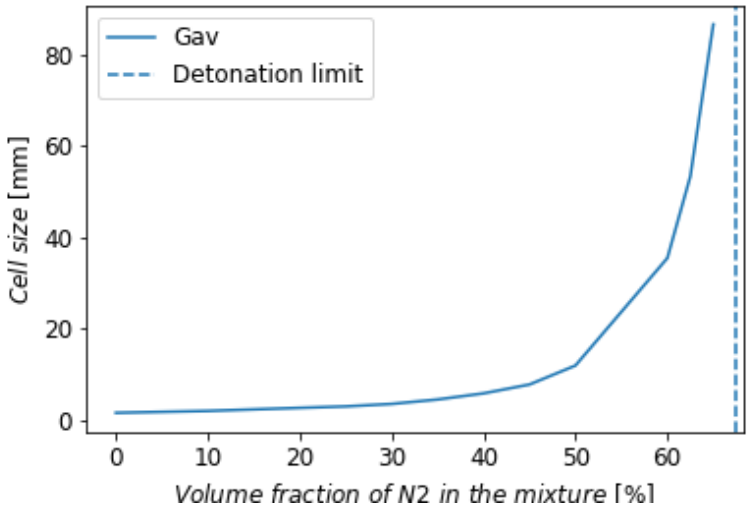

Figure 7: Cell size Gavrikov
Cell size computed with Gavrikov correlation. Significant increase of cell size can be seen when volume fraction of nitrogen is high.

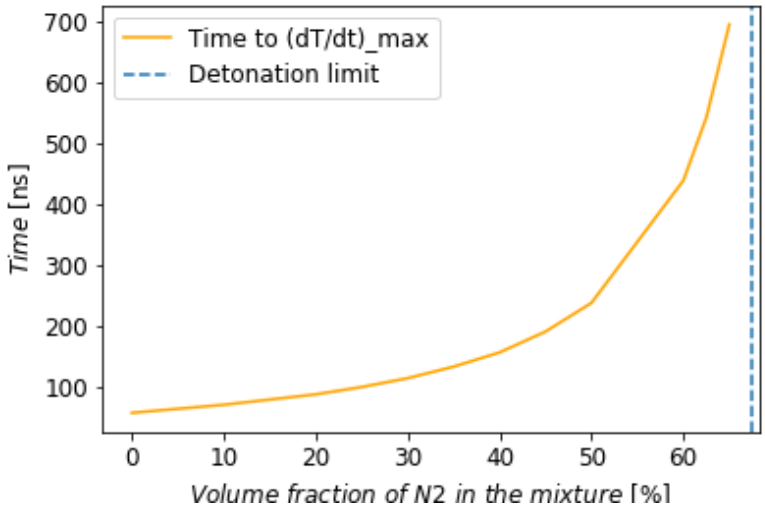

Figure 8: Time to $dT/dt_{(max)}$
Function of induction time in volume fraction of nitrogen. Important value for all detonation studies. It shows how strong and fast detonation will be. Graph is similar to those with detonation cell size and on this graph one can see increasing time of induction due to increasing volume fraction of nitrogen, which is related to cell size, so the model can be assumed as correct.

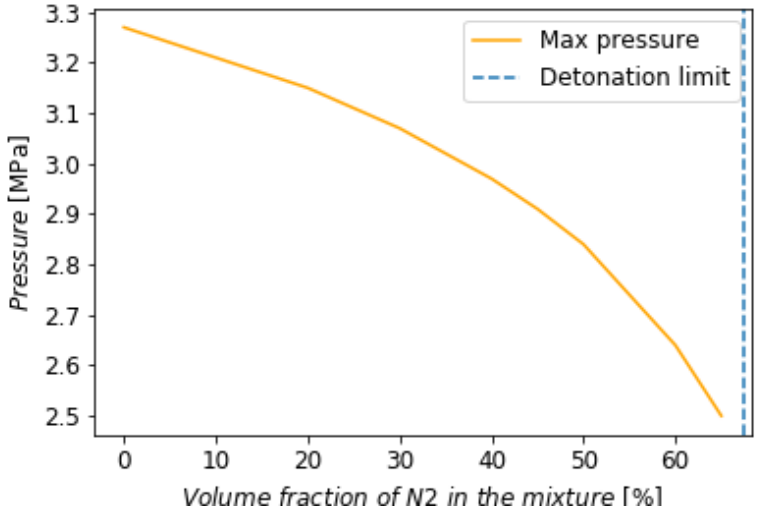

Figure 9: Maximum pressure
Maximum pressure decreases with increase of volume fraction of nitrogen, which is also confirming, that when content of nitrogen in this mixture is higher it gets less reactive.

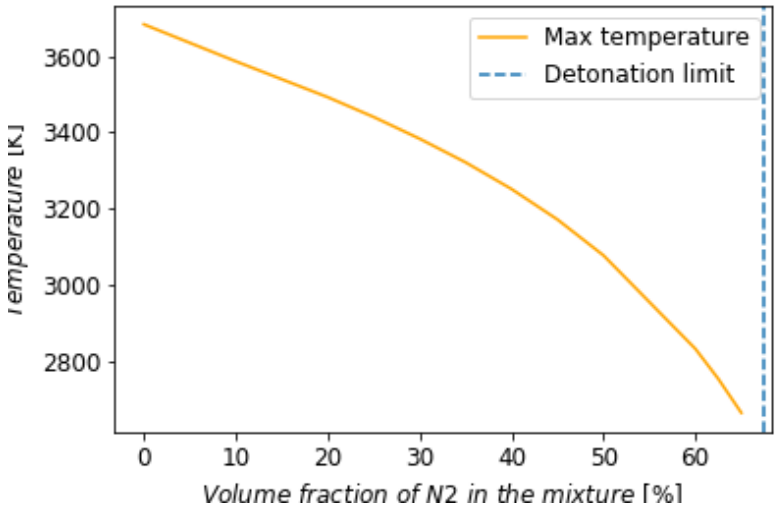

Figure 10: Maximum temperature
Maximum temperature graph can be considered similarly to described pressure graph.

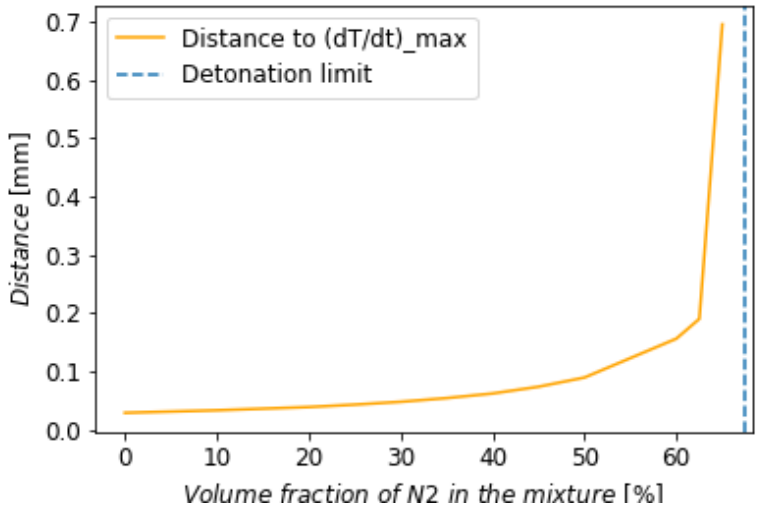

Figure 11: Distance to $dT/dt_{(max)}$
Graph of distance travelled to maximum derivative of temperature - near 60% volume of nitrogen in mixture it is suddenly increasing its value.

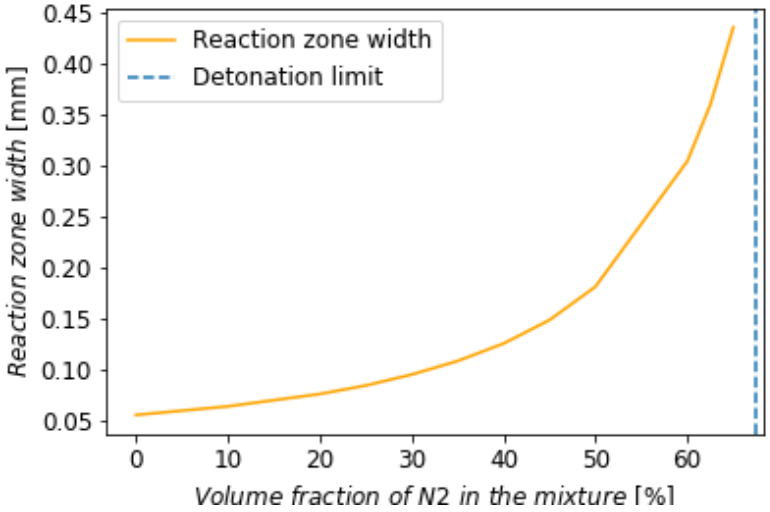

Figure 12: Reaction zone width
Reaction zone width dependent on volume fraction of nitrogen in mixture. The same conclusions can be drawn - if volume fraction of nitrogen is high, reaction zone is wide so the detonation is weak and not so dangerous considering less nitrogen in mixture.

4 Conclusions

As expected, the size of detonation cell is increasing while fraction of nitrogen added to mixture is getting higher. Gavrikov correlation seems to be the most reflecting real process, and this one, from all, is the best described in sources. Increasing detonation cell size means (as mentioned earlier) decreasing reactivity of mixture. The same conclusion can be extracted from pressure and temperature - the higher volume fraction of nitrogen in mixture, the smaller those values are. For induction time graph the conclusion is reversed - higher value means less reactive mixture.

One can clearly notice, that when nitrogen volume is 60% or more, a mixture is comparatively safe, and detonation is not highly possible and dangerous. To prevent situations when detonation of such mixture is possible, one could apply nitrogen to partially empty container and it should alleviate the potential threat of detonation.

References

- $https://github.com/saltazaur/cantera-jupyter/blob/master/demo/demo_ZND_CJcell.py$
- *"Detonation cell widths in hydrogen-oxygen diluent mixtures" R.K.Kumar Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba R0E 1L0, Canada Received 23 February 1989, Revised 7 June 1989*
- *"Hydrogen-air detonations" Guirao, C.M.; Knystautas, R.; Lee, J.H.; Benedick, W.; Berman, M. - Sandia National Labs., Albuquerque, NM (USA); McGill Univ., Montreal, Quebec (Canada); 1982*
- *"Detonation cell size measurements and predictions in hydrogen-air-steam mixtures at elevated temperatures" - G. Ciccarelli, M. Kinoshita; Brookhaven National Laboratory, Department of Advanced Technology, Safety and Risk Evaluation Division, Upton, NY 11973-5000, USA; Received 1 December 1993, Revised 20 April 1994.*
- *"A model for detonation cell size prediction from chemical kinetics" - A.I.Gavrikov; A.A.Efimenko; S.B.Dorofeev - Russian Research Center, Kurchatov Institute, Moscow, Russia - Received 30 May 1998, Revised 21 May 1999*

List of Figures

Python code

```
"""
#############################################################################
Theory, numerical methods and applications are described in the following repo
    Numerical Solution Methods for Shock and Detonation Jump Conditions, S.
    Browne, J. Ziegler, and J. E. Shepherd, GALCIT Report FM2006.006 - R3,
    California Institute of Technology Revised August, 2017
Please cite this report and the website if you use these routines.
Please refer to LICENCE.txt or the above report for copyright and disclaimers.
http://shepherd.caltech.edu/EDL/public/sdt/SD_Toolbox/
#############################################################################
Updated August 2018 - Revised 1/19/2019 to correct Ng Chi parameter definition
Tested with:
    Python 3.5 and 3.6, Cantera 2.3 and 2.4
Under these operating systems:
    Windows 8.1, Windows 10, Linux (Debian 9)
"""
from sdtoolbox.postshock import CJspeed, PostShock_fr, PostShock_eq
from sdtoolbox.znd import zndsolve
from sdtoolbox.cv import cvsolve
import cantera as ct
import numpy as np

def gavrikov(delta,theta,Tvn,T0):
    """
    Correlation function for detonation cell width
    proposed by Gavrikov et al COMBUSTION AND FLAME 120:1933 (2000)
    based on using a reaction zone length based on time to 50limiting
    reactant consumption in constant volume explosion approximation using vn
    postshock velocity to convert time to distance.  Tested against a range
    of fuel-oxidizer diluent mixtures
    INPUT:
        delta = reaction zone length based on time to 50consumption of limiting
        reactant from CV computation and delta = time * w_VN
        theta = Ea/RT_VN,  effective reduced activation energy based on CV
        computation
        Tvn = von Neumann (postshock temperature behind CJ shock wave)
        T0 = initial temperature
    """
    # Constants
    a = -0.007843787493
    b = 0.1777662961
    c = 0.02371845901
    d = 1.477047968
    e = 0.1545112957
    f = 0.01547021569
    g = -1.446582357
    h = 8.730494354
    i = 4.599907939
    j = 7.443410379
```

```
    k = 0.4058325462
    m = 1.453392165
    # Define nondimensional parameters
    X = theta
    Y = Tvn/T0
    z = Y*(a*Y-b) + X*(c*X-d + (e-f*Y)*Y) + g*np.log(Y) + h*np.log(X) + Y*(i/X
    lam = delta*np.power(10,z)
    return lam

def ng(delta,chi):
    """
    Correlation function for detonation cell size from
    Ng, Hoi Dick, Yiguang Ju, and John H. S. Lee. 2007. Assessment of
    Detonation Hazards in High-Pressure Hydrogen Storage from Chemical
    Sensitivity Analysis. INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 32 (1):
    93-99.
    Tested only against low pressure H2-air data.

    INPUT:
        delta = reaction zone length based on peak thermicity in ZND simulatio
        chi = theta*Delta_i/Delta_r where
              theta = reduced effective activation energy from CV computation
              Delta_i = distance to peak thermicity from ZND computation
              Delta_r = w_vN/sigmadot_max from ZND computation

    See Ng et al.  Combustion Theory and Modeling 2005 for a discussion of
    the chi parameter.
    """
    # Constants
    A0 = 30.465860763763;
    a1 = 89.55438805808153;
    a2 = -130.792822369483;
    a3 = 42.02450507117405;
    b1 = -0.02929128383850;
    b2 = 1.0263250730647101E-5;
    b3 = -1.031921244571857E-9;
    lam = delta*(A0 + ((a3/chi + a2/chi)/chi + a1)/chi + ((b3*chi + b2*chi)*ch
    return lam

P1 = 100000; T1 = 300
q = 'H2:2 O2:1 N2:5.57'
mech = 'Mervel2017.cti'
fname = 'h2air'

# Find CJ speed and related data, make CJ diagnostic plots
cj_speed,R2,plot_data = CJspeed(P1,T1,q,mech,fullOutput=True)

# Set up gas object
gas1 = ct.Solution(mech)
gas1.TPX = T1,P1,q
```

```
# Find equilibrium post shock state for given speed
gas = PostShock_eq(cj_speed, P1, T1, q, mech)
u_cj = cj_speed*gas1.density/gas.density

# Find frozen post shock state for given speed
gas = PostShock_fr(cj_speed, P1, T1, q, mech)

# Solve ZND ODEs, make ZND plots
out = zndsolve(gas,gas1,cj_speed,t_end=1e-3,advanced_output=True)

# Find CV parameters including effective activation energy
gas.TPX = T1,P1,q
gas = PostShock_fr(cj_speed, P1, T1, q, mech)
Ts = gas.T; Ps = gas.P
Ta = Ts*1.02
gas.TPX = Ta,Ps,q
CVout1 = cvsolve(gas)
Tb = Ts*0.98
gas.TPX = Tb,Ps,q
CVout2 = cvsolve(gas)
# Approximate effective activation energy for CV explosion
taua = CVout1['ind_time']
taub = CVout2['ind_time']
if taua==0 and taub==0:
    theta_effective_CV = 0
else:
    theta_effective_CV = 1/Ts*((np.log(taua)-np.log(taub))/((1/Ta)-(1/Tb)))

#  Find Gavrikov induction length based on 50% limiting species consumption,
#  fuel for lean mixtures, oxygen for rich mixtures
#  Westbrook time based on 50% temperature rise
limit_species = 'H2'
i_limit = gas.species_index(limit_species)
gas.TPX = Ts,Ps,q
X_initial = gas.X[i_limit]
gas.equilibrate('UV')
X_final = gas.X[i_limit]
T_final = gas.T
X_gav = 0.5*(X_initial - X_final) + X_final
T_west = 0.5*(T_final - Ts) + Ts


for i,X in enumerate(CVout1['speciesX'][i_limit,:]):
    if X > X_gav:
        t_gav = CVout1['time'][i]

x_gav = t_gav*out['U'][0]
for i,T in enumerate(CVout1['T']):
    if T < T_west:
        t_west = CVout1['time'][i]
x_west = t_west*out['U'][0]
```

```
max_thermicity_width_ZND = u_cj/out['max_thermicity_ZND']
chi_ng = theta_effective_CV*out['ind_len_ZND']/max_thermicity_width_ZND
cell_gav = gavrikov(x_gav,theta_effective_CV, Ts, T1)
cell_ng = ng(out['ind_len_ZND'], chi_ng)

print('Mixture:'.format(gas.X))
print('Cell size1 predictions ')
print('Gavrikov correlation = {:8.3e} m'.format(cell_gav))
print('Ng et al correlation = {:8.3e} m'.format(cell_ng))
print('Westbrook correlation = {:8.3e} m'.format(29*x_west))
print('T (K), initial = {:1.5g}, 3,27final = {:1.5g}, max = {:1.5g} K'.format(
print('P (Pa), initial = {:1.5g}, final = {:1.5g}, max = {:1.5g} Pa'.format(ou
print('Time to dT/dt_max = {:8.3e} s'.format(CVout1['ind_time']))
print('Distance to dT/dt_max = {:8.3e} m'.format(CVout1['ind_time']*out['U'][0
print('Reaction zone width (u_cj/sigmadot_max) = {:8.3e} m'.format(max_thermic



"""
Created on Tue Jun 11 21:19:07 2019

@author: JFk
"""
import matplotlib.pyplot as plt

t=[0,10,20,25,30,35,40,45,50,60,62.5,65]


#Cell size

gav=[1.686, 2.1, 2.768, 3.085, 3.625, 4.599, 5.934, 7.873, 12.02, 35.5, 53.36,
ng=[1.986, 2.284, 2.637, 2.929, 3.223, 3.607, 4.16, 4.848, 5.741, 9.466, 11.11
westbrook=[0.8494, 0.9736, 1.136, 1.254, 1.393, 1.575, 1.821, 2.158, 2.617, 4.


plt.clf()
plt.plot(t, gav, label='Gav')
plt.plot(t, ng, label='Ng')
plt.plot(t, westbrook, label='Westbrook')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Cell\ size$ [mm]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Cell size all.png')
plt.show()


plt.clf()
plt.plot(t, gav, label='Gav')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
```

```
plt.legend(loc=0)
plt.ylabel('$Cell\ size$ [mm]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Cell size gav.png')
plt.show()


plt.clf()
plt.plot(t, ng, label='Ng', color='orange')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Cell\ size$ [mm]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Cell size Ng.png')
plt.show()


plt.clf()
plt.plot(t, westbrook, label='Westbrook', color='green')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Cell\ size$ [mm]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Cell size wb.png')
plt.show()

#Temperature
T=[3683, 3586, 3492, 3440, 3383, 3321, 3251, 3171, 3077, 2832, 2753, 2664]

plt.clf()
plt.plot(t, T, label='Max temperature', color='orange')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Temperature$ [K]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('MaxTemp.png')
plt.show()

#Pressure
P=[3.27, 3.21, 3.15, 3.11, 3.07, 3.02, 2.97, 2.91, 2.84, 2.64, 2.57, 2.5]

plt.clf()
plt.plot(t, P, label='Max pressure', color='orange')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Pressure$ [MPa]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('MaxPress.png')
plt.show()

#dT/dt max
```

```
dT_dis=[0.02929, 3.36E-02, 0.03916, 4.33E-02, 0.04813, 0.05449, 0.06236, 0.073
dT_time=[57.62, 70.8, 87.87, 99.92, 114.4, 133.32, 156.6, 190.8, 237.8, 438.5,


plt.clf()
plt.plot(t, dT_time, label='Time to (dT/dt)_max', color='orange')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Time$ [ns]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Time to dTdt.png')
plt.show()

plt.clf()
plt.plot(t, dT_dis, label='Distance to (dT/dt)_max', color='orange')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Distance$ [mm]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Distance to dTdt.png')
plt.show()


#Reaction zone width
RZW=[0.05477, 0.06323, 0.07539, 0.08377, 0.094554, 0.1079, 0.1251, 0.1482, 0.1

plt.clf()
plt.plot(t, RZW, label='Reaction zone width', color='orange')
plt.axvline(x=67.5, ls='--', label='Detonation limit')
plt.legend(loc=0)
plt.ylabel('$Reaction\ zone\ width$ [mm]')
plt.xlabel('$Volume\ fraction\ of\ N2\ in\ the\ mixture $ [%]')
plt.savefig('Reaction zone width.png')
plt.show()
```