Computer methods in combustion

Cantera project

Combustion of gunpowder in a variable volume chamber

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1. Introduction

Gunpowder has been known to mankind since 9^{th} century when it was invented in China. It arrived in Europe in 13^{th} century and was used in weapons ever since. However, it can also serve a purpose in other fields.

The inspiration for this project was application of gunpowder in multi-stage sounding rochets of Students' Space Association of Warsaw University of Technology. It is already widely used for separation of rocket's modules, however there was no way to calculate the needed amount of gunpowder other than tests. This project is an attempt to change it and have a simple way of estimating needed mass, which would then be tested.

2. Theory

Gunpowder is a mixture of potassium nitrate, sulphur and charcoal in proportions of 74%, 10,4% and 15,6% respectively. Sometimes these values differ, however the differences are usually no more than 1%. In this project it is assumed that there are no other species than potassium nitrate, sulphur and carbon that are part of gunpowder. Obviously, that's not true for real gunpowder since all of the components (especially charcoal) are contaminated in real life. The influence of those contaminations is neglected for simplicity of the simulation. It is reasonable as results will be tested anyway.

Combustion of gunpowder is a complicated process and has been an object of research for many years. Today we are sure that there are many reactions that happen simultanously. Again, for simplicity of the simulation one of the approximated models was chosen. It is a commonly cited one-reaction model with very few substances taking part in a reaction:

$$2\,\mathrm{KNO_3} + \mathrm{S} + 3\,\mathrm{C} \longrightarrow \mathrm{K_2S} + \mathrm{N_2} + 3\,\mathrm{CO_2}$$

It is clear that potassium nitrate serves as an oxidizer and coal is a reductor. Sulfur serves a purpose as it binds the potassium. It is consistent with the experiments as sulfur lowers the ignition temerature of gunpowder.

One of the assumptions of this model is complete combustion of carbon as there is no carbon monoxide on the products side.

Characteristics ot this reactions are relatively hard to find in literature. Based on [1], the activation energy of this reaction is $E_a = 13,6\frac{kcal}{mole}$. However, for simulation the reaction rate constant was still needed. It wasn't found in any of the available sources so the approximation was made based on the typical speed of combustion, which is $v = 8\frac{mm}{s}$ (as in [2]). Below is a process of calculating the reaction rate constant.

At first the area of combustion was needed, so it was approximated with the assumption that granules of gunpowder are perfect spheres with a diameter of 1 mm:

$$n\frac{4}{3}\pi(\frac{D}{2})^3 = \frac{m}{\rho}$$

Where n is the number of granules, D — diameter of a granule, m — mass of gunpowder, ρ — density of gunpowder. The surface of combustion is then given by the equation:

$$S = n4\pi(\frac{D}{2})^2 = \frac{6m}{\rho D}$$

Time of combustion of a given mass of gunpowder is expressed by:

$$t = \frac{m}{\rho S v} = \frac{D}{6v}$$

Using a linear approximation rate of change of molar concentration of a given substratum is calculated:

$$\frac{d[A]}{dt} = -\frac{f_A m \rho}{\mu m t} = -\frac{6 f_A \rho v}{D\mu}$$

Where f_A is a mass fraction of a given substratum in gunpowder and μ is a molar mass of a given substratum. Results for each of the substrata are presented below:

$$\frac{d[A]}{dt} = 597270\frac{mol}{m^3 s}$$
$$\frac{d[B]}{dt} = 265200\frac{mol}{m^3 s}$$
$$\frac{d[C]}{dt} = 1060800\frac{mol}{m^3 s}$$

Rate of reaction has then been calculated as:

$$r = -\frac{1}{a}\frac{d[A]}{dt}$$

Where a is a stoichiometric coefficient of a given substratum in the reaction.

Since the approximations of chemical composition of gunpowder and reaction were made the rate calculated for each of the substrates was different so the average was taken as a result:

$$r = 305812\frac{mol}{m^3 s}$$

Since orders of the reaction could not be found in available sources, an assumption was made that they are equal to stoichiometric coefficients. With this assumption reaction rate constant can be calculated as:

$$k = \frac{r}{(\frac{d[A]}{dt}t)^a(\frac{d[B]}{dt}t)^b(\frac{d[C]}{dt}t)^c} = 3,312 \cdot 10^{-20}\frac{m^{15}}{mol^5 s}$$

The coefficent in Arrhenius equation needed for simulation is then calculated assuming the reaction takes place in normal conditions:

$$A = \frac{k}{e^{-\frac{E_a}{RT}}} = 2,679 \cdot 10^{-10}\frac{m^{15}}{mol^5 s}$$

3. Reaction mechanism in Cantera

Since no reaction mechanism was found, one had to be constructed using available knowledge (see section *Theory*). The mechanism was written in a file *nasa.cti* (see section *Attachments*) and contains needed phases, species and a reaction of combustion. Below is a brief description of each of those parts.

Declared phases contain declaration of an ideal gas phase that represents atmospheric air, four stoichiometric solids phases which represent solid substances taking part in a combustion reaction, that is: potassium nitrate, sulfur, carbon and potassium sulfide, an ideal gas phase that represents the gaseous products of combustion (carbon dioxide and nitrogen). Each of tha phases has its characteristics (chemical composition, elements, for solids — constant density). Transport is neglected in this simulation so no model of transport has been implemented. Initial conditions have been set to 300 K and 1 atm. Additionally, the ideal interface has been declared between phases taking part in a reaction. Its initial state is determined by temperature and mass fractions of phases (mass fractions of substrata are equal to their mass fractions in gunpowder and mass fractions of products are set to 0 for achieving stoichiometry).

Species are needed for declaration of phases. All of the declared species have been mentioned in the previous paragraph. Method to determine thermodynamical properties of species is the NASA 9-Coefficient Polynomial Parameterization (coefficents were found in [3]). No transport model has been implemented.

The declared reaction is the same as in *Theory* section. It is a surface reaction that is meant to happen on an interface.

Unfortunately, despite many tries, the reaction mechanism still doesn't work and throws an error of undeclared species although all of them are clearly listed in the file.

4. Simulation

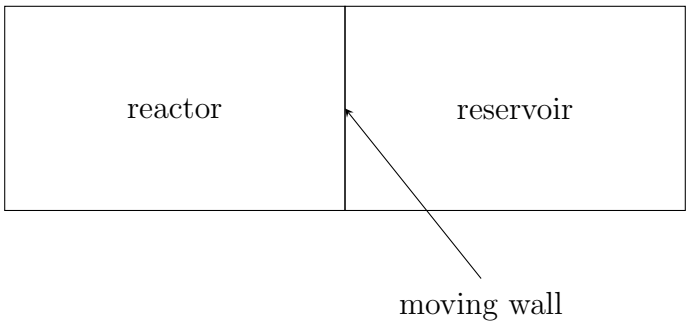

Figure 1: Model of a system used for simulation

Figure 1 presents a simple model that was used for this simulation. Reactor contains all of the combustion substrata ad products as well as the interface. The reservoir is meant to simulate the atmosphere, it has constant pressure and temperature and is filled with air. Between the reactor and a reservoir there is a moving wall. Its movement is dependent on difference of pressure.

The python code is presented in *project.py* file (see section *Attachments*). Its input is defined at the beginning and conntains: mass of gunpowder, frotal area of a piston (moving wall), mass of the piston, timestep of a simulation, initial length of a reactor, final length of a reactor as well as the input file with reaction mechanism.

At first all substaces are declared using phases from input file. Their initial state is set (just in case) and quantities of substances taking part in a reaction are defined. The interface between phases is also declared with initial state of 500 K, which should be enough to start the reaction.

Then the phases are added to the reactor (or reservoir in case of air) and initial reactor volume is set using frontal area of a piston and initial length of a reactor. Wall is added with the area as set in the input and a constant of proportionality between velocity and pressure difference is set to timestep times area divided by mass of the piston. Reactors and wall are then added to a reaction network.

Then the output file is initialised and the simulation begins. Current simulation time is printed in the output window and temperature, pressure, and volume of the reactor as well as velocity of the wall are saved in the output file.

Simulation is ended if the volume of the reactor exceeds a product of area of the piston and final length of the piston or (to prevent infinite loop in case of any unforseen error) after 120 seconds.

5. Conclusion

Although the project isn't working properly because of an unknown Cantera error, its educational value is of great importance and since this simulation may have a practical application, work on it hasn't ended yet.

However, the precision of calculations may be questionable since a lot of approximations have been made. The reason of this is lack of precice research on parameters of the reaction. It is very surprising as gunpowder has been known to mankind for a very long time.

6. Bibliography

1. *Thermoanalytical study of the ignition and combustion reactions of black powder* by Clement Campbell and Garry Weingarten, Pyrotechnics Laboratory, Picatinny Arsenal, Dover, New Jersey (20^{th} May, 1959)

2. *Pressure dependence of the burning rate of black powder* — translation of an article by O. I. Leypunskiy in Journal of Physical Chemistry, Moscow, 1960

3. NASA ThermoBuild (`https://cearun.grc.nasa.gov/cea/index_ds.html`)

4. Cantera 2.3.0 documentation (`https://www.cantera.org/docs/sphinx/html/index.html`)

7. Attachments

1. File *nasa.cti* — Cantera input file with reaction mechanism

2. File *project.py* — Cantera code with simulation