

# Deflagration-to-Detonation Transition in Mixtures of the Pyrolysis Products of Polypropylene with Air

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## 1 Introduction

Currently, one of the possible solutions of the problem of increasing the energy efficiency of the combustion process in power plants of high-speed aircraft is associated with the development of detonation engines [1]. In such engines, the chemical energy of the fuel is converted into useful expansion work due to fuel combustion in the controlled detonation mode. The corresponding thermodynamic cycle is referred to as the Zel'dovich cycle [2]. In this paper, we propose to solve this problem using controlled detonation of the gaseous pyrolysis products of solid fuel in the air. Until now, such an approach has been considered only in relation to deflagrative combustion [3–7].

The most important property which determines the perspectives for the use of solid fuels in a detonation engine is their detonability. The relative detonability of fuel–air mixtures (FAMs) is usually estimated by the energy of direct detonation initiation and by the cell size of the multifront detonation. The determination of these parameters is fraught with difficulties and with large measurement errors.

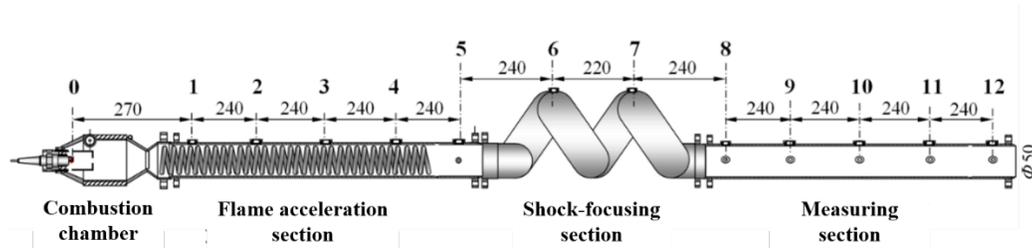


Figure 1. Schematic of PDT with indication of measuring segments:  
0 - ignition point, 1–12 - sections with IPs and/or PSs

## 2 Experimental Setup and Procedure

Based on our previous studies [8], we propose a new method for determining the detonability of various fuels: by the deflagration-to-detonation transition (DDT) run-up length and/or time under the same conditions using a pulsed detonation tube (PDT). In addition to PDT, the test bench includes an air supply system, a gas generator, a mixer, as well as control devices, ignition system and data acquisition system based on ionization probes (IPs) and high-frequency pressure sensors (PSs).

The PDT includes (Fig. 1) a combustion chamber and three sections: the flame acceleration section, the shock-focusing section and the measuring section. Compressed air is periodically fed into the mixer, in which it is mixed with a combustible gas, continuously coming from the gas generator. The mass flow rate of air is determined by the change in pressure in the air receiver. The mass flow rate of a combustible gas is estimated by the time of complete decomposition of the solid fuel sample in the gas generator. From the mixer, the FAM is fed to the PDT combustion chamber, where it is ignited by a standard automobile spark plug. The formed flame passes into the flame acceleration section equipped with the 900-mm long Shchelkin spiral wound from steel wire 6 mm thick with a pitch of 24 mm.

Behind the flame acceleration section, there is a shock-focusing section in which gas-dynamic focusing of compression waves occurs and spontaneous exothermic centers appear, which ultimately can lead to the fast DDT according to the mechanism of [9] and further detonation propagation. The shock-focusing section is a tube twisted in two turns. The outer diameter of the section is 136 mm, the inner diameter is 36 mm, and the pitch of the turns is 220 mm.

The measuring section of the PDT is a straight smooth-walled tube designed to measure the parameters of the resulting deflagration and detonation waves. An additional section of a 1790 mm long tube is attached to the end of this section, directing the combustion products to the ventilation system (not shown in Fig. 1).

The PDT diagram of Fig. 1 shows the numbers of the control and measuring sections – the locations where IPs and PSs are installed – and the distances between them. There are 12 such sections along the length of the tube. In sections 1–7 and 10, only IPs are installed, and in sections 8, 9, 11, and 12, both IPs and PSs are installed. The principle of operation of the IP and measurement methods are described in [10]. With the help of the IP, the instantaneous position of the flame is determined with an accuracy of  $\pm 2$  mm. Using PSs, the instantaneous position of the pressure wave is determined with an accuracy of  $\pm 6$  mm.

The recyclable granulated polypropylene (GP) is used as solid fuel. The thermal decomposition of GP occurs in the gas generator, a cylindrical stainless-steel reactor with a height of 280 mm and a diameter of 60 mm. The gas generator is placed in a muffle furnace heated to the decomposition temperature  $T_d$ , which is controlled by a thermocouple with an accuracy of  $\pm 5$  °C.

The characteristics of the gas generator are determined in the temperature range of  $650\text{ }^{\circ}\text{C} \leq T_d \leq 800\text{ }^{\circ}\text{C}$  with a weight of the GP sample of 15 g. With an increase in decomposition temperature, the characteristic pressure rise time and total decomposition time decrease. The characteristic time to maintain pressure at a constant level is 40%–50% of the total decomposition time. The maximum absolute pressure of gases in the gas generator depends on  $T_d$ , increasing from 0.2 MPa at 650 °C to 0.3 MPa at 800 °C.

Chromatographic analysis of the composition of the gaseous pyrolysis products of GP showed that they mainly consist of propylene  $\text{C}_3\text{H}_6$ , isobutene  $\text{iso-C}_4\text{H}_8$ , ethane  $\text{C}_2\text{H}_6$ , methane  $\text{CH}_4$ , ethylene  $\text{C}_2\text{H}_4$  and propane  $\text{C}_3\text{H}_8$ . Table 1 presents examples of the analysis with indication of the mass content of the main products in the gas phase for several values of  $T_d$ . For products with 4 ( $\text{C}_4$ ) and 5 ( $\text{C}_5$ ) carbon atoms, the numbers in parentheses are the total values of the concentration of products except for isobutene and 2-methylbutene-1. The relative accuracy of determining the composition of the products is  $\pm 5\%$ .

Experiments on determining the detonability of a FAM are carried out according to the following procedure. First, a cyclogram of the test-bench operation is set. The operation cycle is adjusted assuming that the combustible gas is supplied to the PDT continuously, and the air is supplied in portions. The duration of the air supply is selected according to its mass flow rate so that the volume of gases supplied to the detonation tube is greater than the volume of the tube. After ignition, the air supply stops for a short time and then resumes. The break in the air supply is aimed at providing a “plug” of the pyrolysis products between the new batch of fresh FAM and the combustion products of the previous cycle. After that, the cycle with air supply, ignition and the break are repeated a specified number of times (“shots”). The unit operates autonomously until complete decomposition of solid fuel in successive shots.

The air-to-fuel mass ratio  $L_o$  are determined based on the mass flow rates of air and combustible gas. Recall that for stoichiometric FAMs based on hydrocarbons such as aviation kerosene  $L_{o,st} \approx 15$ . Knowing the  $T_d$  and  $L_o$ , as well as the initial air temperature  $T_a \approx 20^{\circ}\text{C}$ , it is possible to estimate the temperature of the FAM at the inlet of PDT:  $T_m \approx (T_d + L_o T_a)/(1 + L_o)$ .

Figure 2 shows an example of primary recordings of IPs (dashed curves) and PSs (solid curves) for one of the shots in the experiment with the FAM based on the products of the GP pyrolysis. The countdown of time starts from the moment of ignition. The moments of sharp deviation of IP records down from the zero line correspond to the arrival of the flame front at a control section (see point and arrow for section 5). Similarly, the moments of sharp deviations of the PS records up from the zero line correspond to the arrival of a pressure wave at a control section (see point and arrow for section 8). Knowing the distances of all control sections from the ignition source, based on Fig. 2, it is possible to plot the dependences of the flame front and pressure wave velocities on the distance traveled and determine the DDT run-up length  $L_{DDT}$  and time  $t_{DDT}$ . According to [11], detonation occurs where the time delay between the arrival of the pressure wave and the flame front does not exceed  $\sim 100\text{ }\mu\text{s}$ , i.e. FAM self-ignites due to shock compression. In sections 8, 9, 11 and 12, there is virtually no time delay between the IP and PS signals, i.e. a detonation wave propagates in the measuring section. In this example,  $L_{DDT} \approx 2\text{ m}$  and  $t_{DDT} \approx 15\text{ ms}$ .

Table 1: Composition of polypropylene pyrolysis products (% mass)

N	$T_d$ , °C	$\text{C}_3\text{H}_6$	$\text{iso-C}_4\text{H}_8$ ( $\text{C}_4$ )	$\text{C}_2\text{H}_6$	$\text{CH}_4$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_8$	2-Me- Buten-1 ( $\text{C}_5$ )	$\text{H}_2$	Rest
1	650	38.8	14.1 (3.2)	12.1	10.2	9.7	3.8	1.2 (3.9)	0.3	9.8 (2.7)
2	650	40.8	14.5 (3.5)	10.7	7.9	8.2	3.8	1.5 (5.3)	0.1	12.5 (3.7)
3	800	27.7	10.7 (4.1)	10.1	21.3	17.7	2.6	0.3 (1.8)	2.0	7.7 (1.7)
4	800	30.4	11.2 (4.0)	10.2	19.4	16.8	2.8	0.6 (1.9)	1.9	6.7 (0.8)

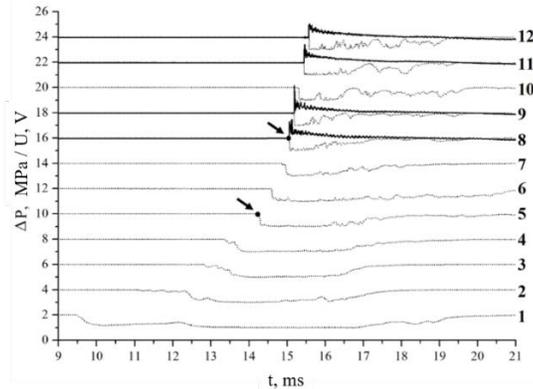


Figure 2. Primary records of IPs (voltage  $U$  in V) in control sections 1–12 (dashed curves) and PSs (overpressure  $\Delta P$  in MPa) in control sections 8, 9, 11 and 12 (solid curves) for one shot in the experiment with FAM based on the GP pyrolysis products at a decomposition temperature of 700 °C

### 3 Results and Discussion

Table 2 shows the results of typical experiments with DDT in the FAM based on the products of GP pyrolysis at  $650\text{ °C} \leq T_d \leq 800\text{ °C}$ , as well as experiments with the stoichiometric FAMs based on methane and LPG of the PBA (propane-butane automobile) brand. Experiments with methane and LPG were conducted to debug the methodology and to obtain comparative data. In addition, other gaseous fuels (hydrogen, acetylene, propane, propylene, etc.) were tested, but the corresponding results are not discussed herein. Unlike the pyrolysis products of GP, which were fed to the PDT in a heated state, the FAMs based on methane or LPG were fed to the PDT at room temperature. Table 2 shows all the most important parameters of the experiments and the results of measurements of  $L_{DDT}$  and  $t_{DDT}$ , as well as the mean values of the measured detonation velocity.

Experiments 38, 39 and 40 were conducted at  $T_d \approx 700\text{ °C}$ . It is seen from Table 2 that the value of  $L_o$  in experiments 38, 39, and 40 decreased from 13.5 to 11. If one considers that  $L_{o,st} \approx 15$ , then in all these experiments, the FAM is enriched with fuel: the air-to-fuel equivalence ratio  $\alpha = L_o/L_{o,st} < 1$ . The temperature of the FAM at the inlet to the PDT in these experiments is  $T_m \approx 75\text{ °C}$ .

Figure 3 demonstrates how flame accelerates in the PDT from shot to shot on the example of experiment 40. It shows the dependences of the flame front and pressure wave velocities on the distance traveled for six successive shots 2 to 7. All six shots exhibited detonation, i.e., DDT with the subsequent propagation of the detonation wave at an apparently constant velocity on the level of 1700–1870 m/s was recorded in the measuring section of the PDT. In all the shots, DDT occurred between sections 7 and 8 at the exit from the shock-focusing section, i.e.  $L_{DDT} \approx 2\text{ m}$ . Despite the change in the composition of the FAM from shot to shot, the DDT run-up length  $L_{DDT}$  changed only slightly. In runs 38 and 39, the same values of  $L_{DDT}$  were obtained. As for the DDT run-up time, it turned out to be minimal in experiment 38 ( $t_{DDT} \approx 10.6\text{ ms}$ ) and maximum in experiment 40 ( $t_{DDT} \approx 11.7\text{ ms}$ ), i.e. enrichment of FAM with fuel, as expected, reduced its detonability.

In experiments 59 and 61 conducted at  $T_d \approx 650\text{ °C}$  and  $800\text{ °C}$ , DDT followed by detonation wave propagation in the measuring section of PDT at a quasistationary velocity on the level of 1650–1800 m/s and 1650–1900 m/s, respectively, were also recorded. In these experiments, DDT also occurred between sections 7 and 8 at the exit from the shock-focusing section of the PDT, i.e.  $L_{DDT} \approx 2\text{ m}$ . If one compares

Table 2: Results of several experiments on DDT in FAMs based on methane, LPG, and pyrolysis products of GP

No of exp. / fuel	89 <sup>†</sup> LPG	59 <sup>**</sup> GP	38 GP	39 GP	40 GP	61 <sup>***</sup> GP	82 <sup>†</sup> methane
Decomposition temperature, $T_d$ , °C	-	653	705	703	710	804	-
Initial air pressure in receiver, MPa	-	0.37	0.40	0.37	0.33	0.40	-
Final air pressure in receiver*, MPa	-	0.31	0.37	0.33	0.30	0.33	-
Ai flow rate (mean), g/s	-	2.5	2.7	2.4	2.2	2.9	-
Fuel flow rate (mean), g/s	-	0.2	0.2	0.2	0.2	0.26	-
Mass air-to-fuel ratio, $L_0$	15.3	12.1	13.5	11.8	11.2	11.0	17.3
Air-to-fuel equivalence ratio, $\alpha$	1.00	0.81	0.90	0.79	0.74	0.74	1.00
Relative mass of solid residue, %	-	4.9	7.3	7.3	7.3	18.0	-
Number of shots	6	8	8	10	6	6	6
Estimated FAM temperature at PDT inlet, $T_m$ , °C	20	68	74	73	77	85	20
$L_{DDT}$ , m	~2	~2	~2	~2	~2	~2	~2
$t_{DDT}$ , ms	12.9	12.9	10.6	11.2	11.7	8.6	15.1
Mean detonation velocity, m/s	1800	1730	1800	1800	1800	1770	1715

\* Equilibrium pressure after 5 min.; \*\* Sampling, shot #5 (see Table 1, No.1); \*\*\* Sampling, shot #6 (see Table 1, No. 4); † - experiment 89 and 82 with premixed FAM

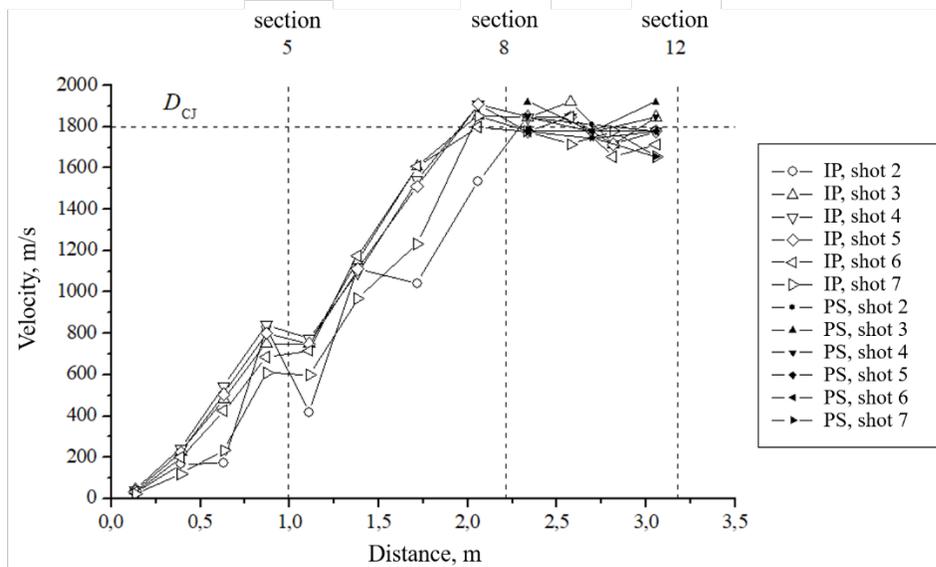


Figure 3. The dependences of the flame front and pressure wave velocities on the distance traveled for six successive shots 2–7 in experiment 40 with FAM based on the pyrolysis products of GP

the DDT run-up time in experiments 59, 40 and 61, it turns out to be minimal in experiment 61 ( $t_{DDT} \approx 8.6$  ms) and maximum in experiment 59 ( $t_{DDT} \approx 12.9$  ms), i.e. increase in the decomposition temperature  $T_d$  from 650 to 800 °C increases the detonability of the FAM.

In experiments with the FAMs of stoichiometric composition based on methane and LPG, DDT was also obtained at  $L_{DDT} \approx 2$  m, however the DDT run-up time  $t_{DDT}$  was 13 and 15 ms, respectively. Moreover, an unstable limiting (spinning) detonation mode was registered in the methane–air mixture with detonation decay in the measuring section. This means that the detonability of FAM based on pyrolysis products of GP at decomposition temperatures  $T_d$  ranging from 650 to 800 °C is comparable or even exceeds the detonability of the stoichiometric FAM based on LPG under normal conditions.

#### 4 Concluding remarks

Thus, we have proposed a new method for determining the detonability of a fuel based on the measured values of the DDT run-up length and time in PDT. The most important feature of the PDT is its operation in a pulse-periodic mode: air and pyrolysis products of solid fuel are fed into the reaction volume and periodically ignited with a predetermined frequency, so that enough statistics are gathered in one experiment to determine the DDT run-up length and time. GP is selected as a solid fuel. A test bench with PDT was designed and manufactured together with a gas generator for obtaining the pyrolysis products of GP at a decomposition temperature of up to 800 °C. Chromatographic analysis of the products showed that they mainly consist of propylene C<sub>3</sub>H<sub>6</sub>, isobutene iso-C<sub>4</sub>H<sub>8</sub>, ethane C<sub>2</sub>H<sub>6</sub>, methane CH<sub>4</sub>, ethylene C<sub>2</sub>H<sub>4</sub> and propane C<sub>3</sub>H<sub>8</sub>. A set of experiments on the DDT in air mixtures of GP pyrolysis products has been performed. It has been shown that in mixtures with air enriched in fuel ( $0.73 \leq \alpha \leq 0.90$ ), at normal pressure and elevated initial temperature (70–90 °C), the products of GP pyrolysis exhibit detonability close to that of LPG in a stoichiometric mixture with air under normal conditions.

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#### References

- [1] Zel'dovich YaB (1940) To the question of energy use of detonation combustion. *Sov. J. Tech. Phys.* 10(17):1455.
- [2] Frolov SM, Aksenov VS, Ivanov VS. (2015) Experimental proof of Zel'dovich cycle efficiency gain over cycle with constant pressure combustion for hydrogen–oxygen fuel mixture. *Int. J. Hydrogen Energy.* 40(21):6970.
- [3] Zvuloni R, Gany A, Levy Y (1988) Geometric effects on the combustion in solid fuel ramjets. *J. Propulsion.* 5(1):32.
- [4] Lv Z, Xia ZX, Liu B, Liu YC. (2015) Experimental and numerical investigation of a solid-fuel rocket scramjet combustor. *J. Propulsion Power.* 1:6.
- [5] Vnuchkov DA., Zvegintsev VI, Lukashevich SV, Nalivaichenko DG. (2017) The method for determination of solid fuel combustion characteristics in high-speed air flow. *Combustion and Explosion.* 10(4):51.
- [6] Hadar I, Gany A (1992) Fuel regression mechanism in a solid fuel ramjet. *Propellants, Explosives, Pyrotechnics.* 17:70.
- [7] Pei X, Wu Z, Wei Z, Liu J. (2013) Numerical investigation on internal regressing shapes of solid-fuel scramjet combustor. *J. Propulsion Power.* 29(5):1041.
- [8] Frolov SM, Aksenov VS, Basevich VYa. (2006) Initiation of heterogeneous detonation in tubes with coils and Shchelkin spiral. *High Temperature.* 44(2):283.
- [9] Frolov SM. (2005) Initiation of strong reactive shocks and detonation by traveling ignition pulses. *J. Loss Prevention Proc. Ind.* 19(2-3):238.
- [10] Frolov SM, Aksenov VS, Dubrovskii AV, Zangiev AE, Ivanov VS, Medvedev SN, Shamshin IO. (2015) Chemiionization and acoustic diagnostics of the process in continuous- and pulse-detonation combustors. *Doklady Physical Chemistry.* 465(1):273.
- [11] Basevich VYa, Frolov SM, Posvyanskii VS. (2005) Existence conditions of stationary heterogeneous detonation. *Rus. J. Chemical Physics.* 24(7):58.