THE ETHANOL REFORMING IN DOUBLE-PULSE DISCHARGE IN A PLASMA-LIQUID SYSTEM WITH CYLINDRICAL GEOMETRY

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Talk outline

***Motivation*:**

Plasmachemistry + “Green” Chemistry →
Pulsed plasma-liquid systems (PPLS)

***Experimental*:**

Pulse plasma-liquid systems of cylindrical geometry with the focusing of shock waves.

***Methodology*:**

Research and diagnostics of pulse plasma-liquid systems: current, pressure, emission spectroscopy of plasma and FTIR spectroscopy of gas exhaust.

***Basic results*:**

Current and acoustics in modes of the single and dual pulses. Reforming ethanol.

Conclusion

Plasmachemistry → “Green” Chemistry

<u>Traditional way of increasing a plasma-chemical selectivity is transferring from thermal to non-equilibrium plasma (</u>XX century)<u>.</u>

Today, the need to increase the selectivity of the plasma chemistry become strong by the transition of the chemical industry to "green chemistry". "Green Chemistry" is a departure from the traditional concept of evaluating the effectiveness of the chemical yield to the concept that evaluates the cost-effectiveness as the exclusion of hazardous waste and non-toxic and / or hazardous substances [Sheldon R. A. C. Rus. Chem. J., 48 (2004) 74-83].

“GREEN” CHEMISTRY PROCESSES

Perspectives towards green chemistry have processes in supercritical fluids (water, carbon dioxide). For example, in supercritical water significantly increases the rate of oxidation, such as the use of water can be not only effective destruction of hazardous chemical substances, but also hydrolysis, hydration, formation or degradation of carbon-carbon bonds, and so on. One of the most interesting uses of the supercritical water - effectively destroying chemical warfare agents [Robert W. Shaw-CB MTS IV (2002)].

Critical parameters of different solvents

• Solvent	Molecular mass	Critical temperature, Tcrit	Critical pressure, Pcrit	Critical density, ρcrit
	g/mol	K	MPa (bar)	g/sm^3
CO_2	44.01	303.9	7.38 (72.8)	0.468
H_2O	18.015	647.096	22.064 (217.755)	0.322
ethanol	46.07	513.9	6.14 (60.6)	0.276

Problem of "Green" Chemistry

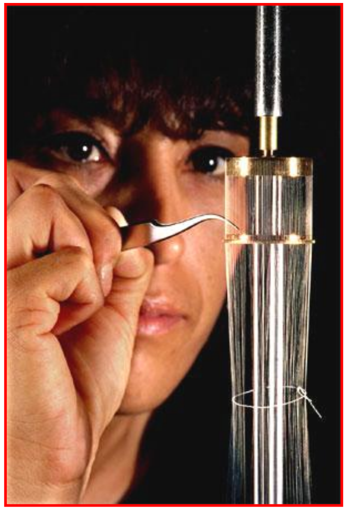
The main problem that hinders the introduction of technologies with supercritical water - it's pretty high cost industrial units, working under high pressure: they need heat-resistant alloys and special accessory, which eliminates the possibility of explosions reactors. In addition, scH_2O - aggressive environment, it causes strong corrosion of parts.

A possible solution to this problem:

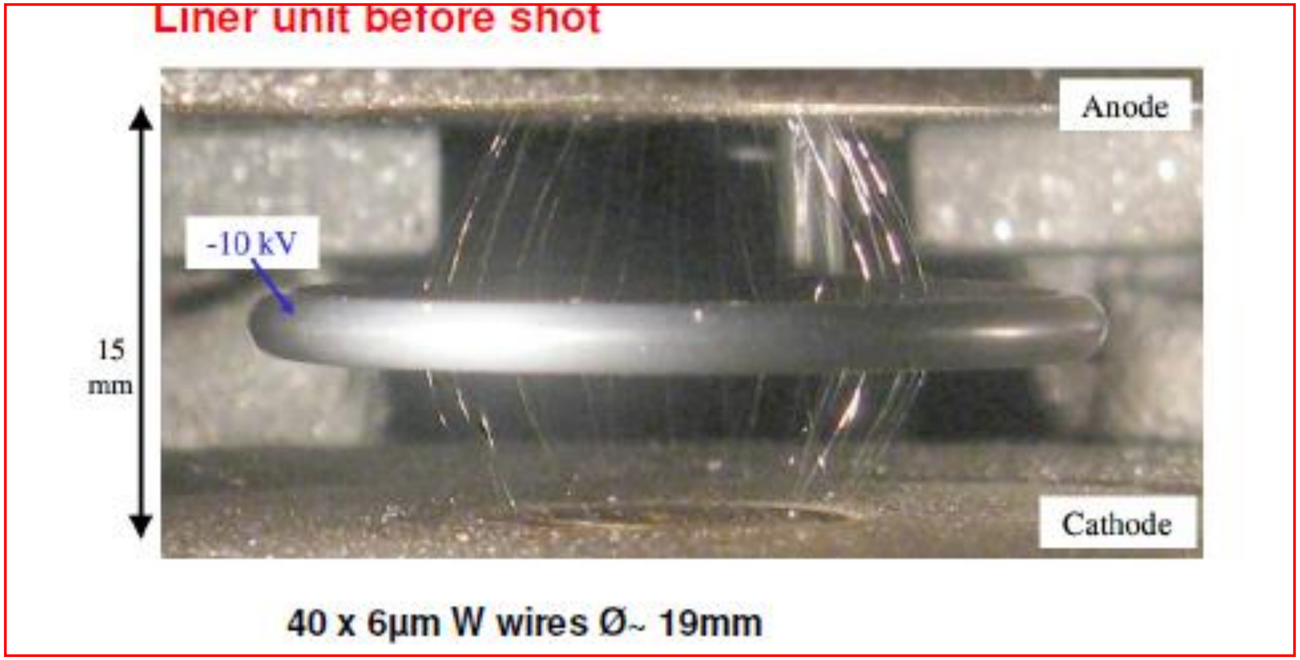
Implementation conditions supercritical liquid in collapse convergent acoustic waves can be a solution to the problem of extreme aggressiveness of scH_2O.

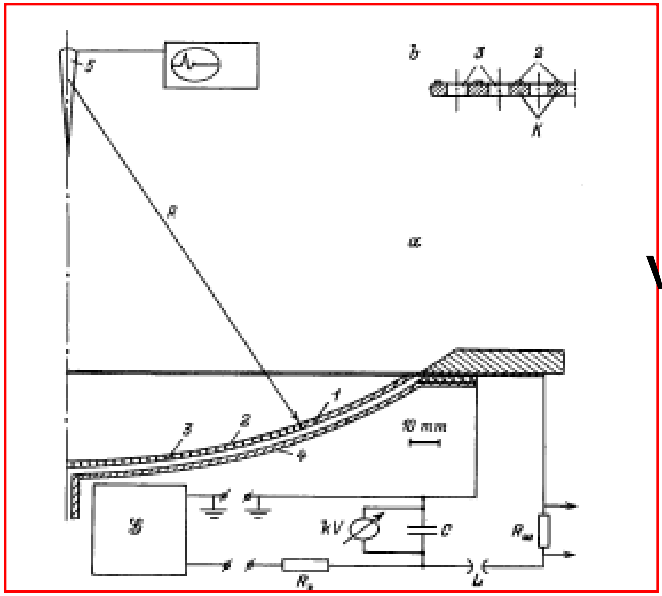
The principal feature of most approaches to the implementation of the collapse of converging cylindrical and spherical shock waves – nonideal symmetry of the initial shock wave due to the discreteness of the energy input and the lack of synchrony of energy input to the wave front.

Chris Deeney at all



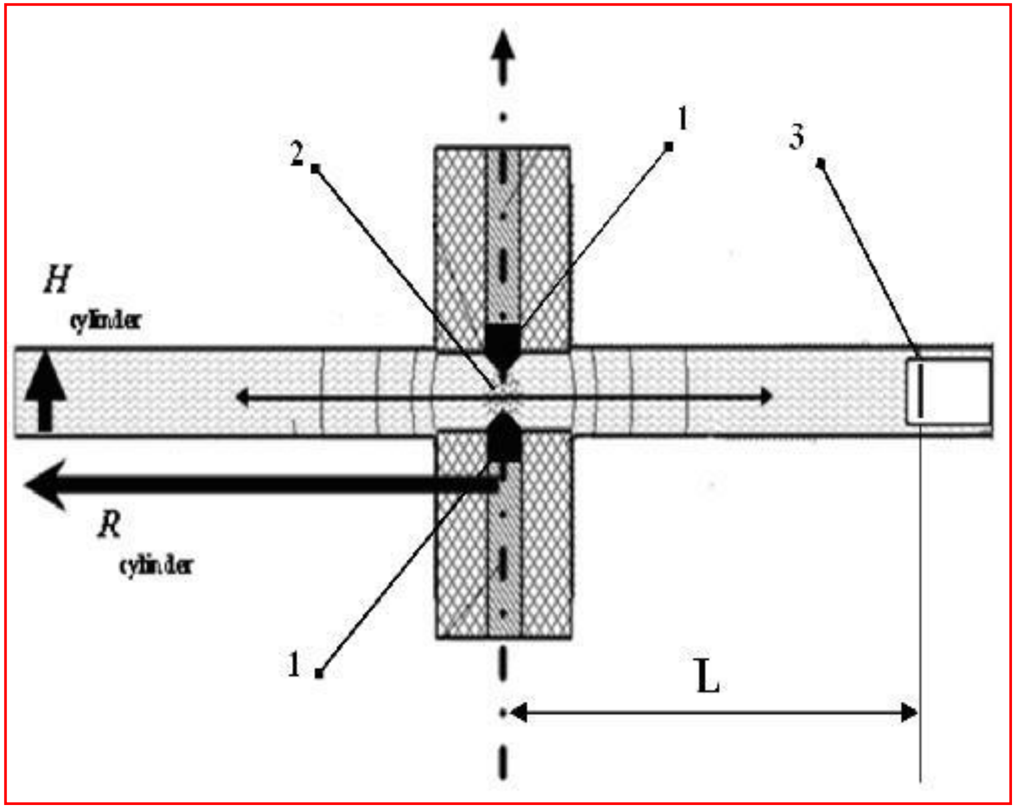
E.V. Grabovski at all JIHT RAN, Russia





V.S. Teslenko at all IGD Sibirian Branch RAN, Russia

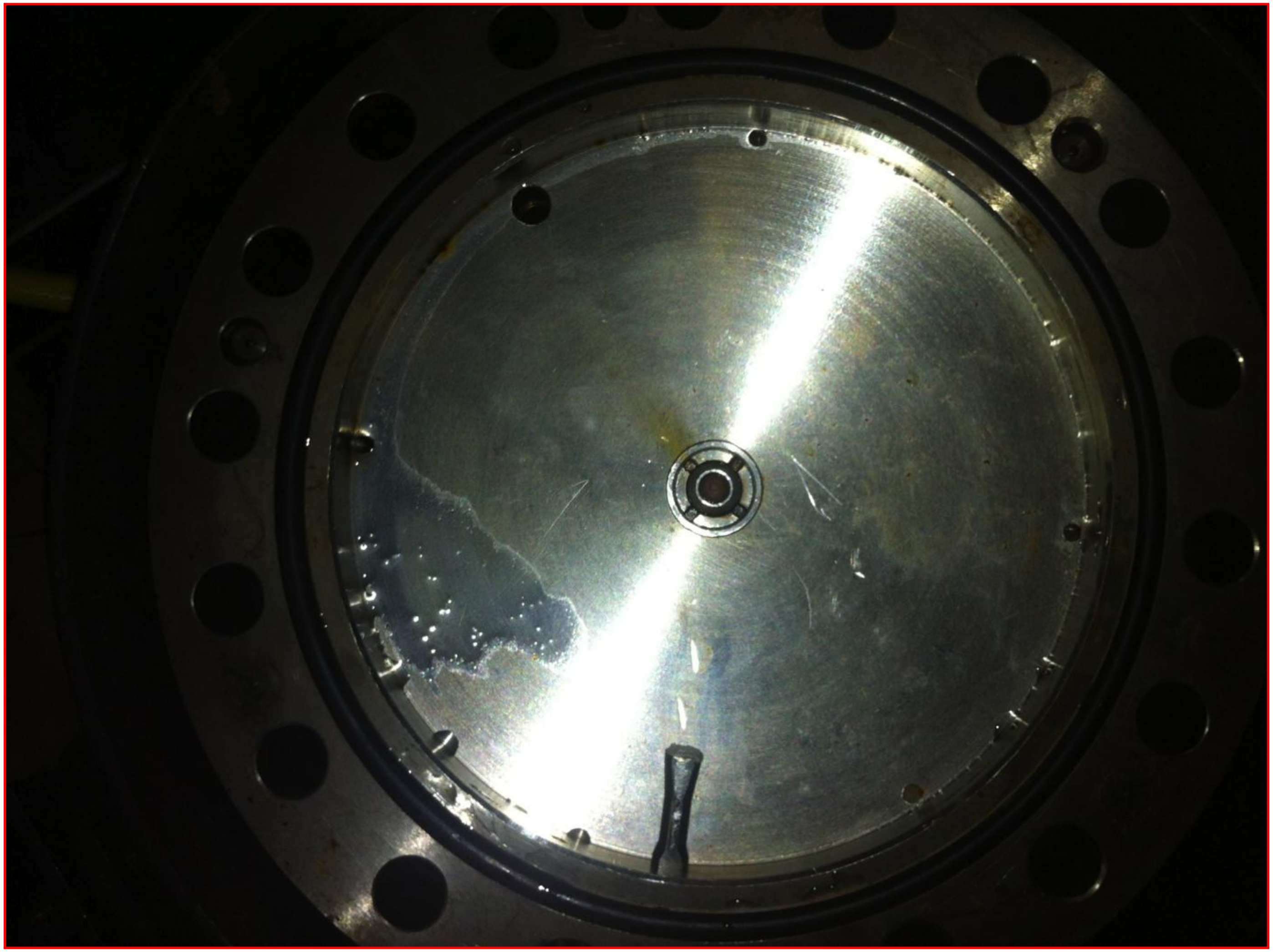
CYLINDRICAL PLASMA-LIQUID SYSTEM



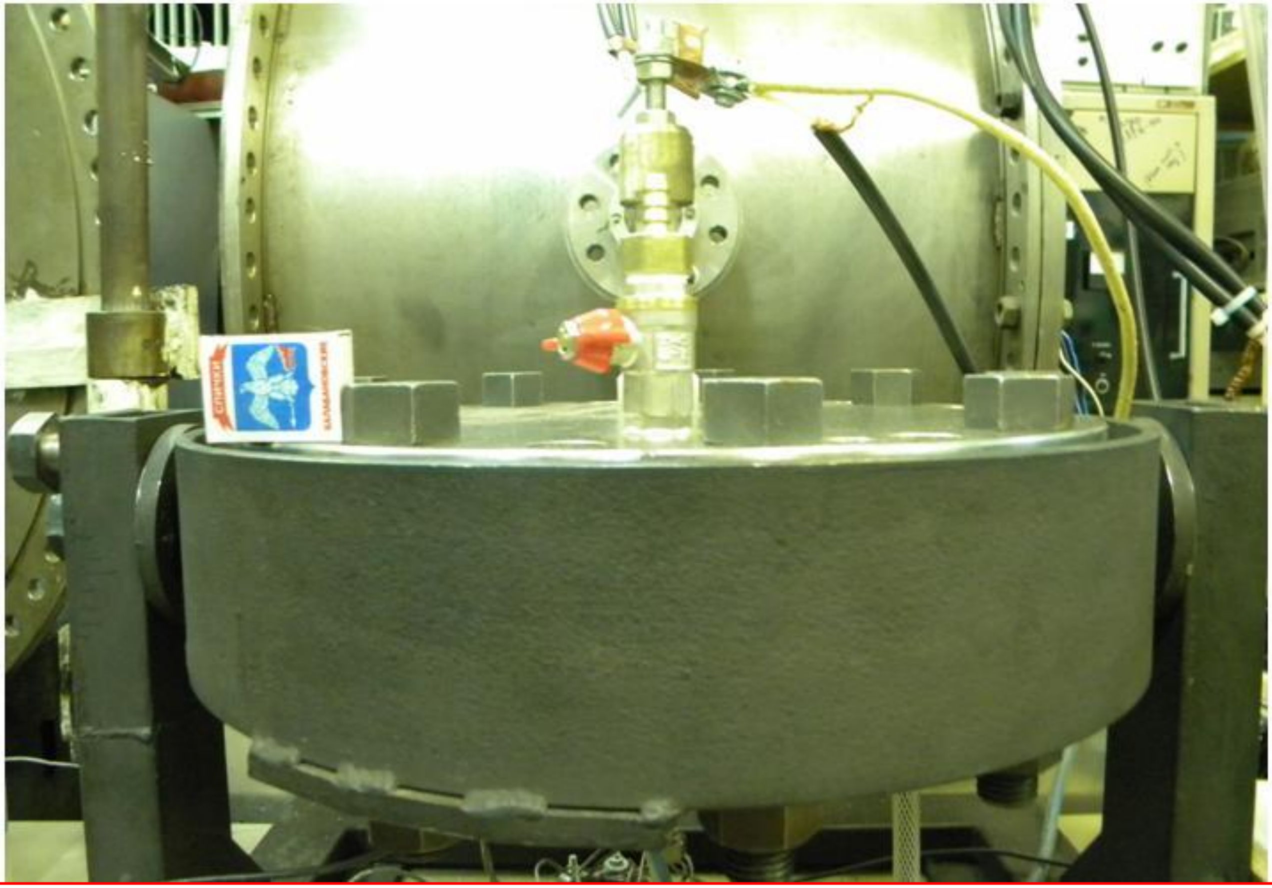
R / H = 13.5

Experimental plasma chemical reactor (base radius is much greater than the height of the cylinder) 1 — metal electrodes, 2 — discharge plasma, 3 — piezoceramic pressure sensor.

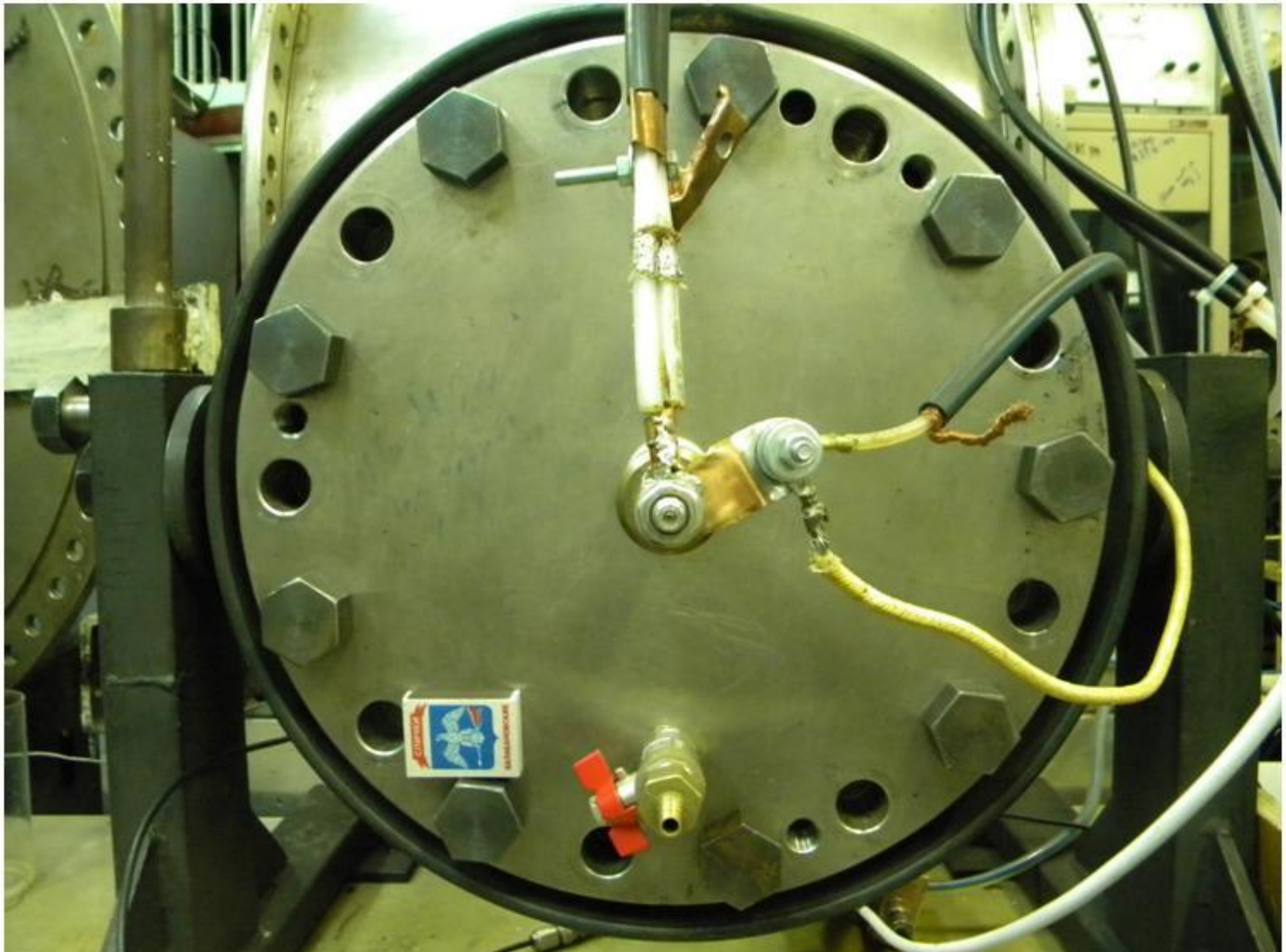
Experimental plasma chemical reactor



Experimental plasma chemical reactor (horizontal cylinder)

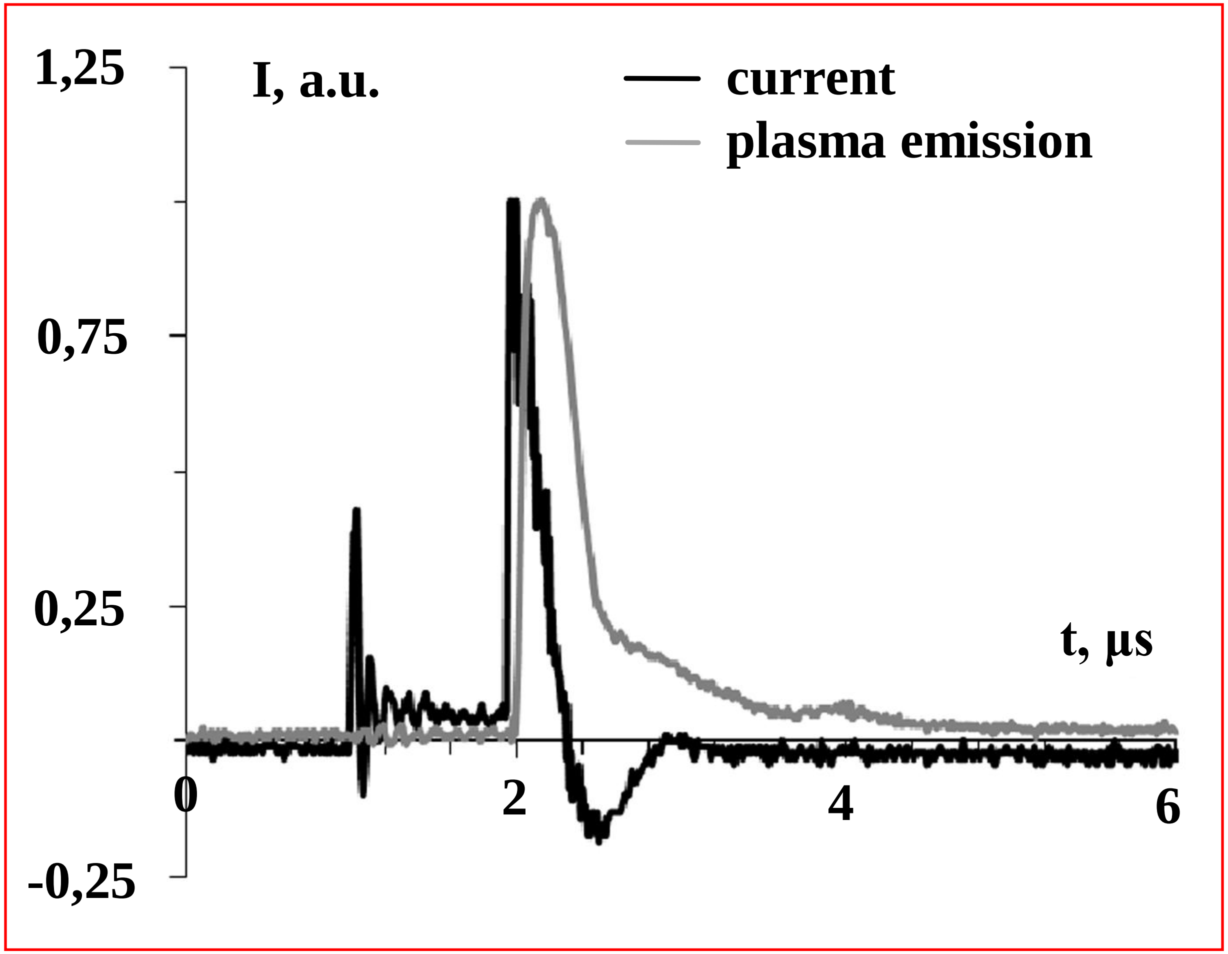


Experimental plasma chemical reactor (vertical cylinder)

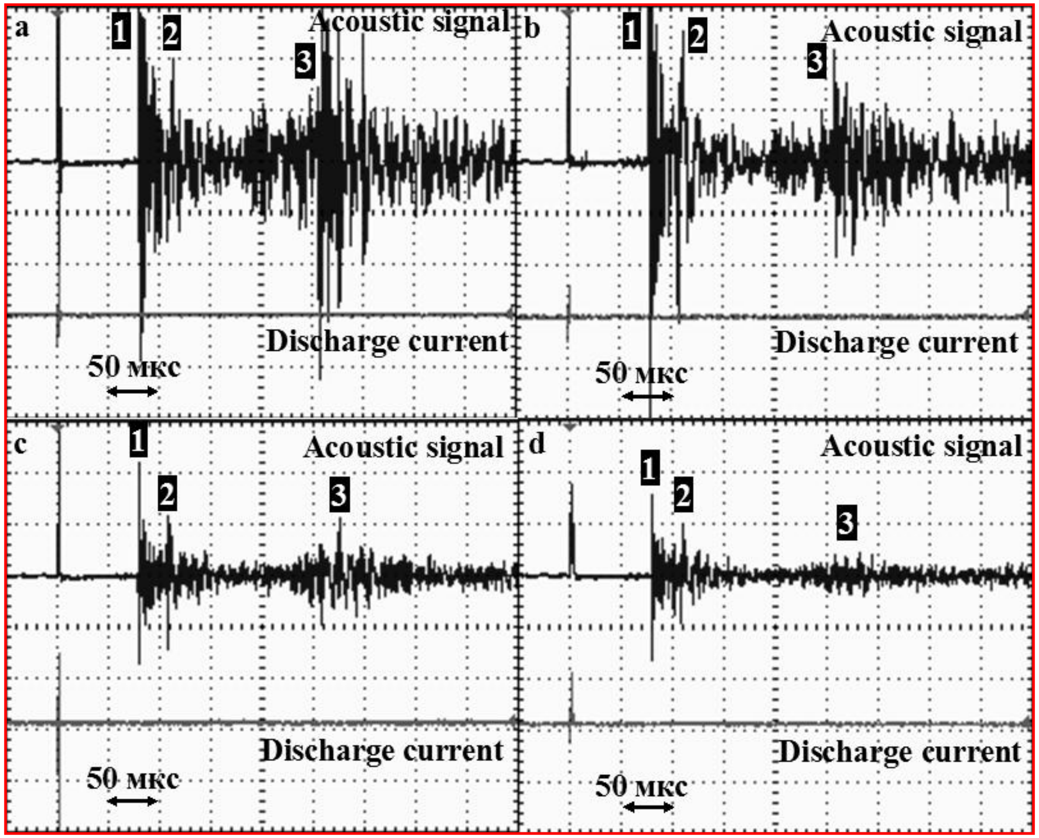


Experimental plasma chemical reactor (vertical cylinder)

Oscillogrames of discharge current and plasma emission (water, C=0.015 μF, without air, ballast resistance R=10 Ohm)



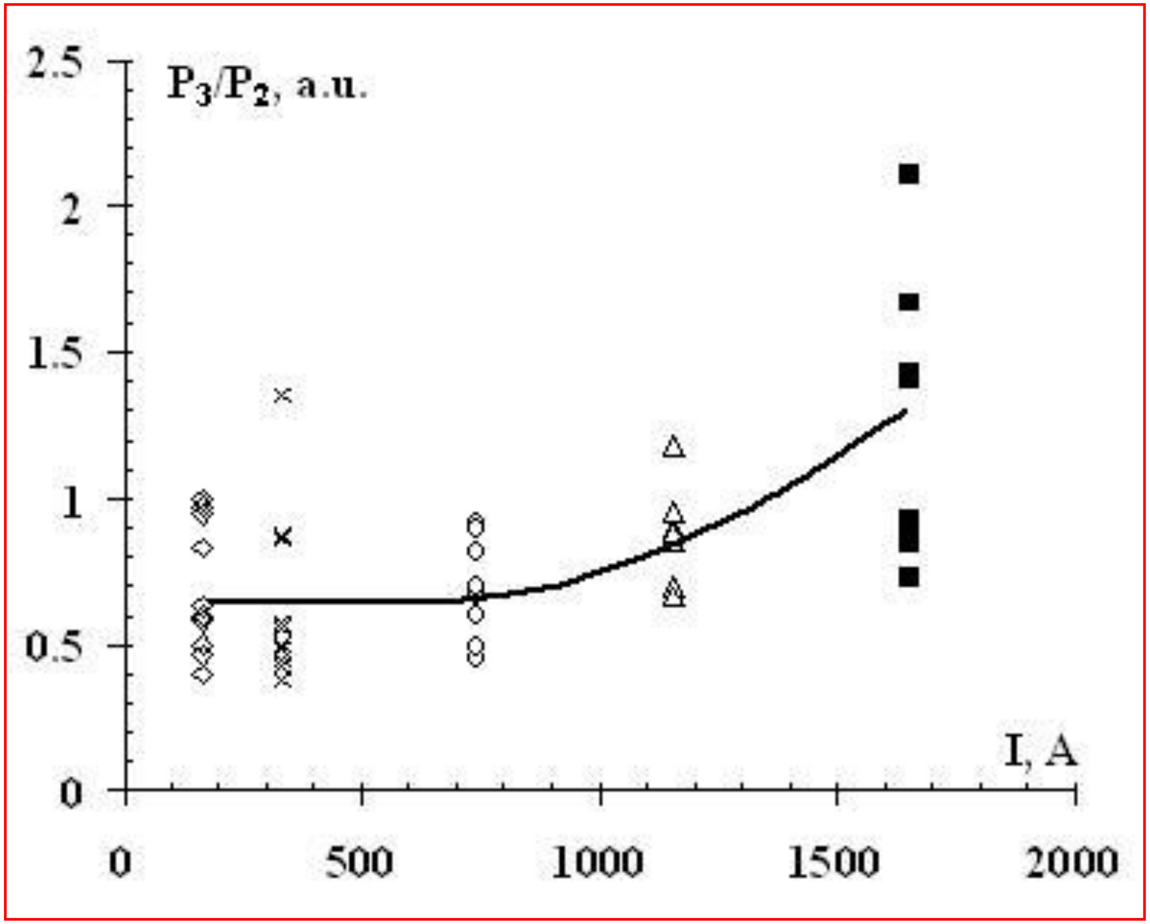
Oscillogrammes of current and acoustic signal in mode of the single pulses



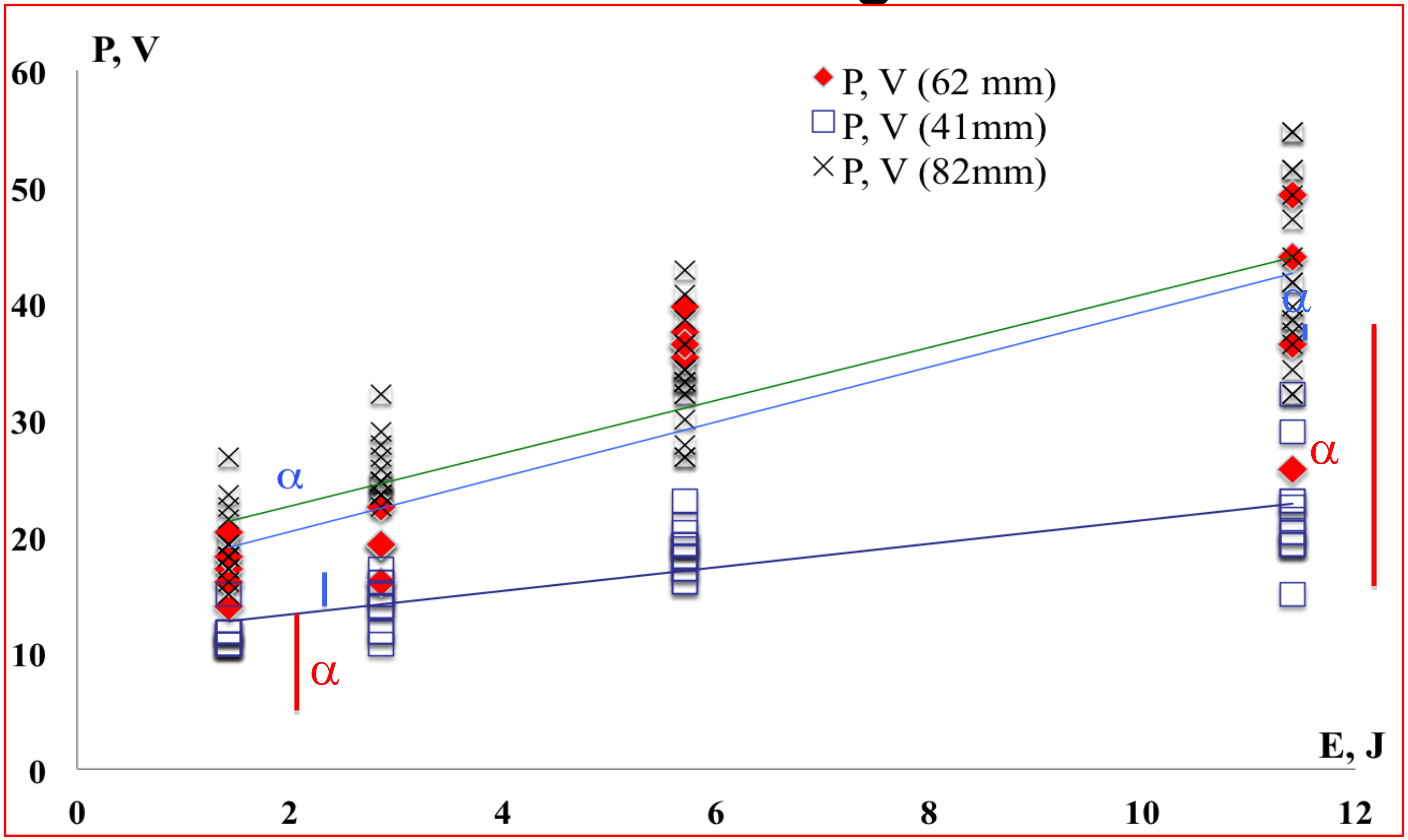
R_{balast}: a — 0 Om, b — 10 Om; c — 20 Om, d — 50 Om, sensitivity P – 0.5 V/div. Tap water with flow 4 cm^3/s, without incoming gas flow, d=0,5 mm, C=0,015 μF, U=19,5 kV, horizontal cylinder. 1 - first divergent acoustic wave; 2 - first convergent acoustic wave; 3 - second divergent acoustic wave.

The dependence of the ratio of the amplitude of the second divergent wave (3) to the amplitude of the first convergent wave (2) on the pulse current

(Indices 2 and 3 correspond to indices previous slide)



Radial distribution of the amplitudes of acoustic signals



Due to the cumulation effect the pressure of the converging SW [*shock wave*] grows according to a power law:

[1.G. S. Sarkisov, S. E. Rosenthal, K. W. Struve and D. H. McDaniel, PRL 94, 35004 (2005). 2. Grinenko, V. Tz. Gurovich, Ya. E. Krasik, A. Sayapin, S. Efimov and J. Felsteiner, Analysis of shock wave measurements in water by a piezoelectric pressure probe, Rev. Sci. Instr. 75, 240 (2004). 3. A. Sayapin, A. Grinenko, S. Efimov, and Ya. E. Krasik, Comparison of different methods of measurement of pressure of underwater shock waves generated by electrical discharge, Shock Waves, s00193-06-0011-8, (2006).]

Initial energy

$$P_{sw} \propto \frac{E_T}{R_0^{\beta}} R_{sw}^{-\alpha} = B R_{sw}^{-\alpha}$$

Initial radius

α ~ 1.33 - spherical implosion

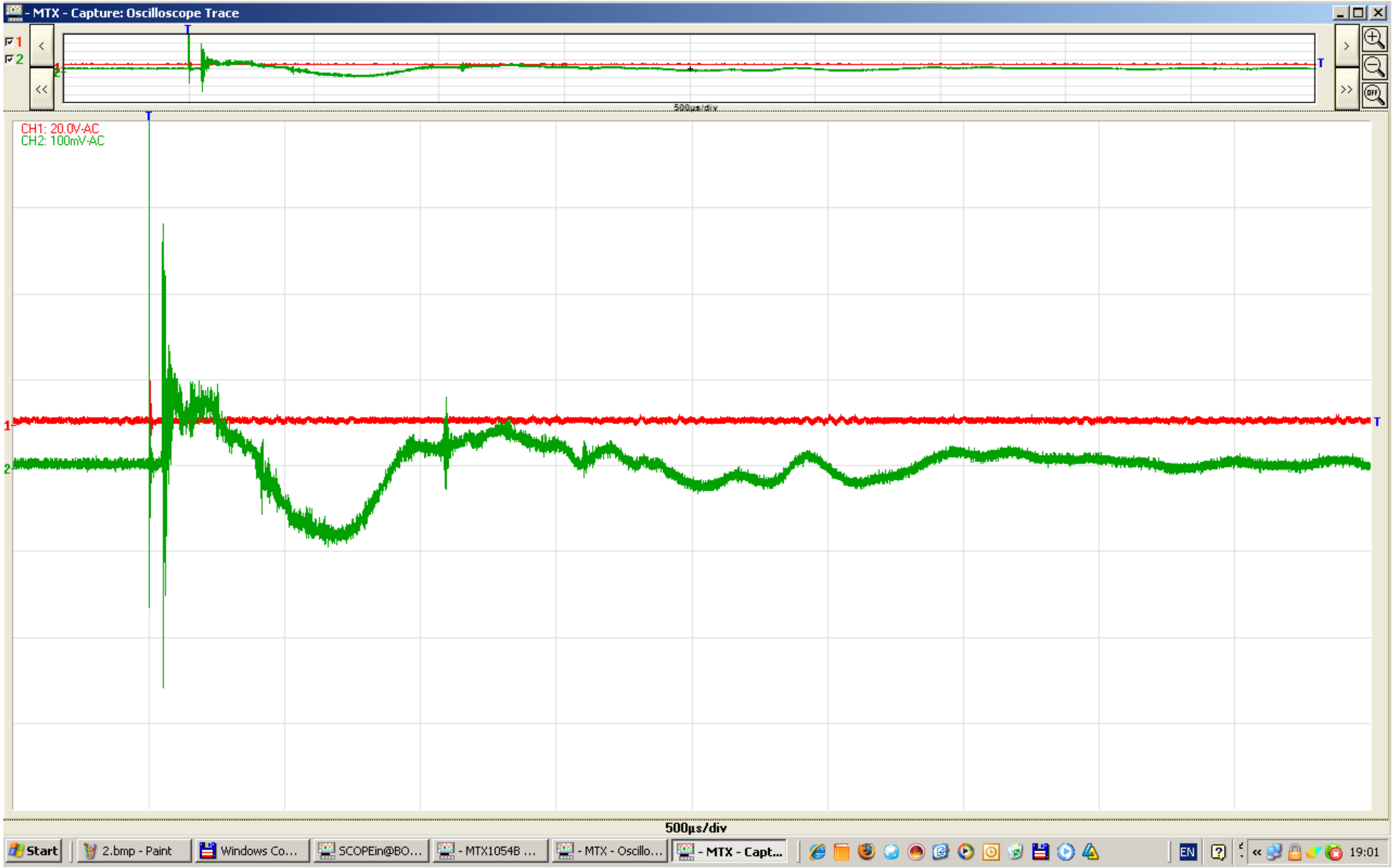
α ~ 0.67 - cylindrical implosion

The pressure of the divergent AW (acoustic wave):

$$P_{aw} = AR_{aw}^{-\alpha}$$

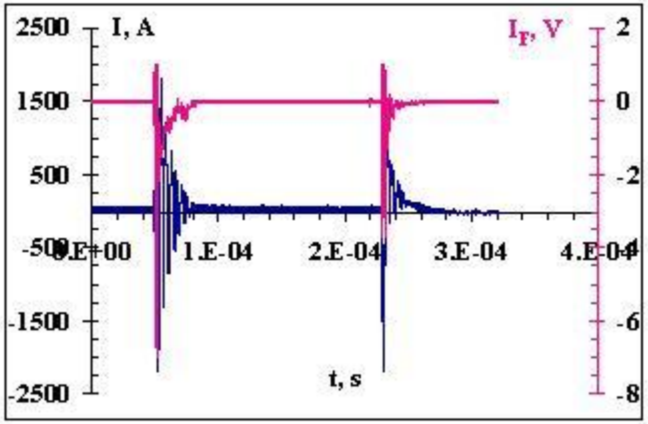
	P_{sw} (literature)	P_{aw} (KNU)
α - cylinder	0,67	1,58 ÷ 2 1 ÷ 1,1
α - sphere	1,33	

Oscillograms of the discharge current (red) and the acoustic signal (green).
C = 30 nF, U = 19,5 kV,R = 0 Om

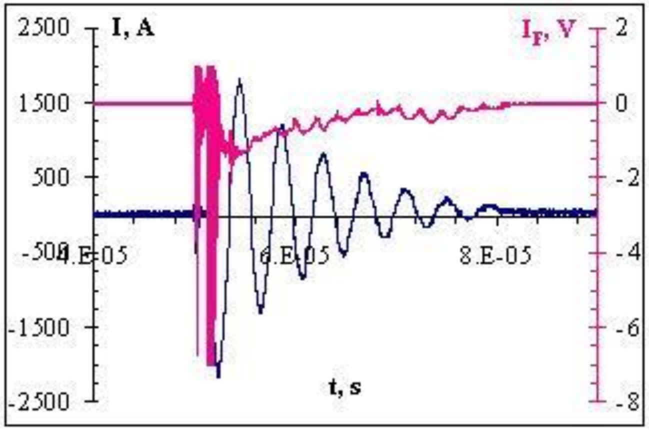


Oscillogrammes of current and plasma emission in mode of the double pulses (C_1 - 12J;C_2 – 17J)

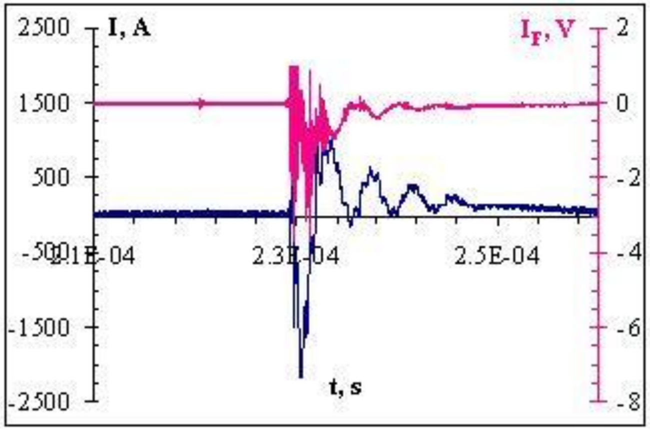
a)



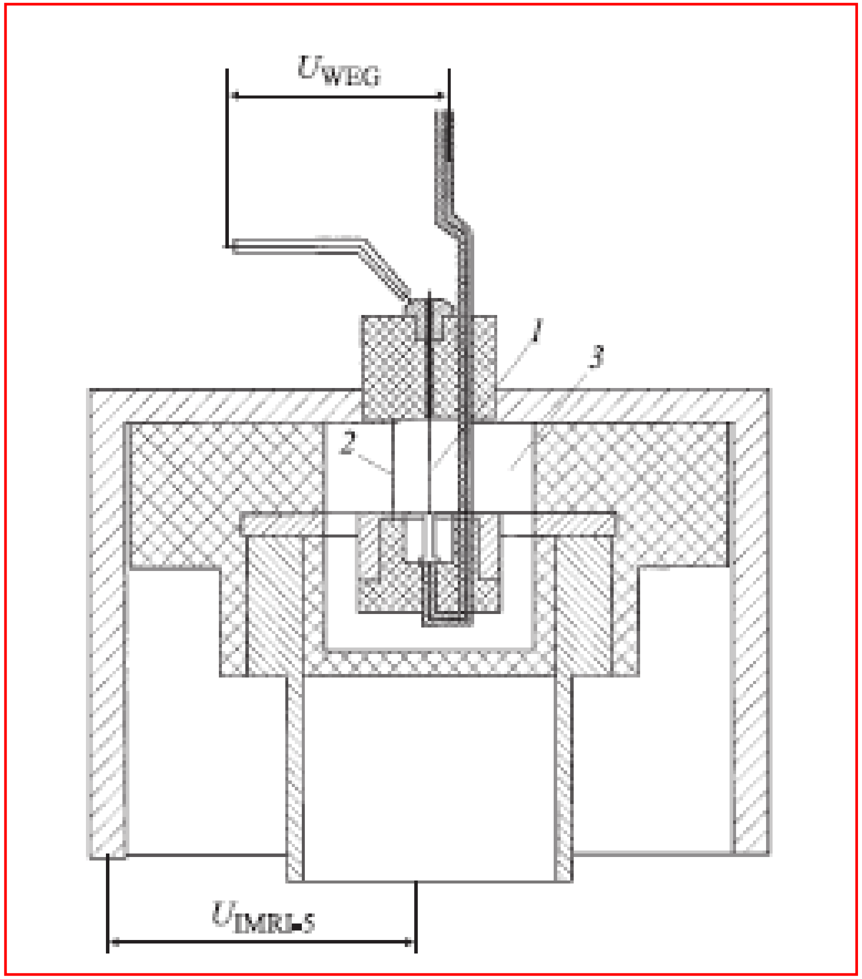
b)



c)



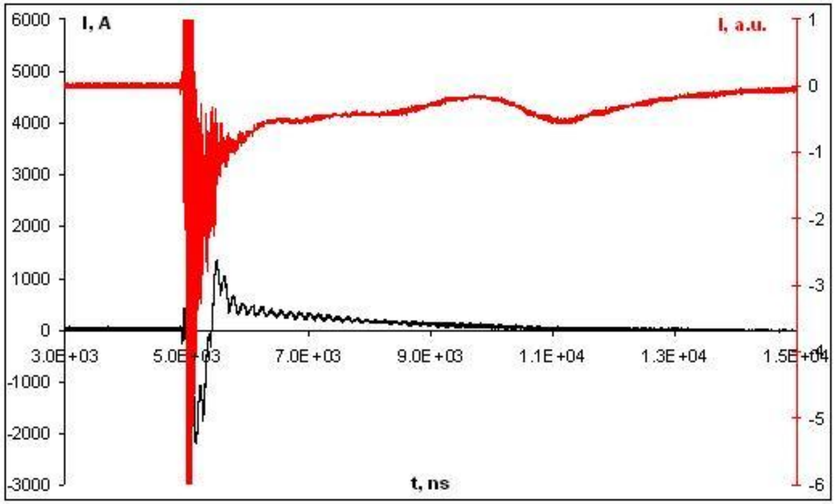
A.G. Russkikh, V.I. Oreshkin, A. Yu. Labetsky, S.A. Tchaikovsky, A. Shishlov. IHCE Sibirian Branch RAN, Russia (2007)

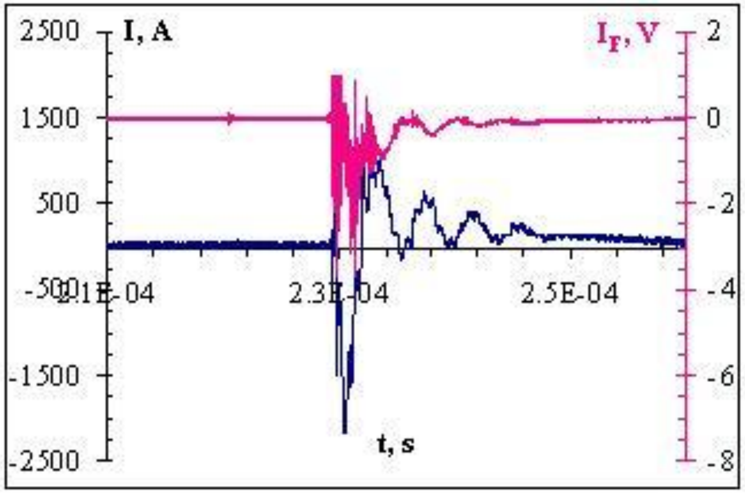


1 - tungsten wire diameter of 30 µm,
2 - stranded cascade D=16,3 mm, L=2 cm (28 copper wires with a diameter of 150 µ m),
3 - distilled water.
U=74 kV, C = 3.23 µF, E=10 kJ, I == 0.5 MA.

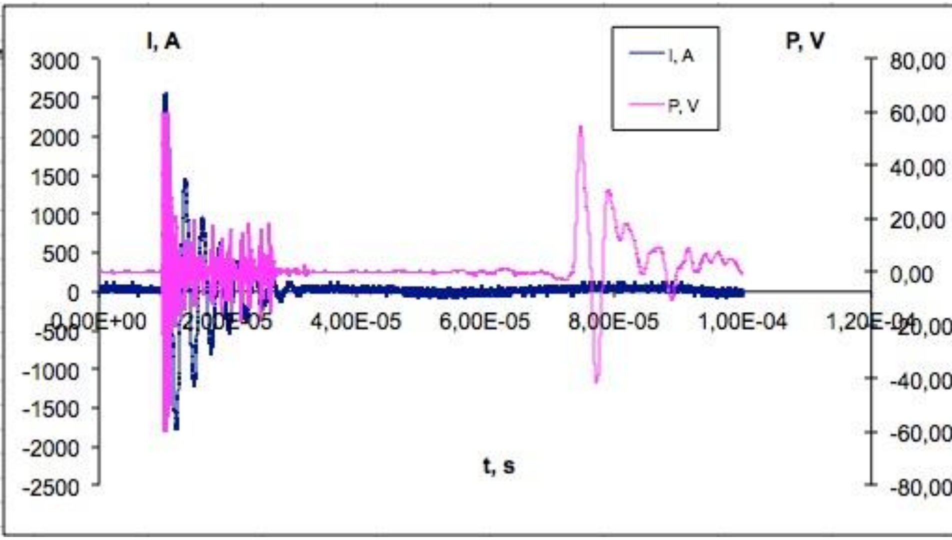
Oscillogrammes of current and plasma emission in mode of the single (a) and double pulses (b) with C_2 – 17J (Rb = 0)

a) **b)**

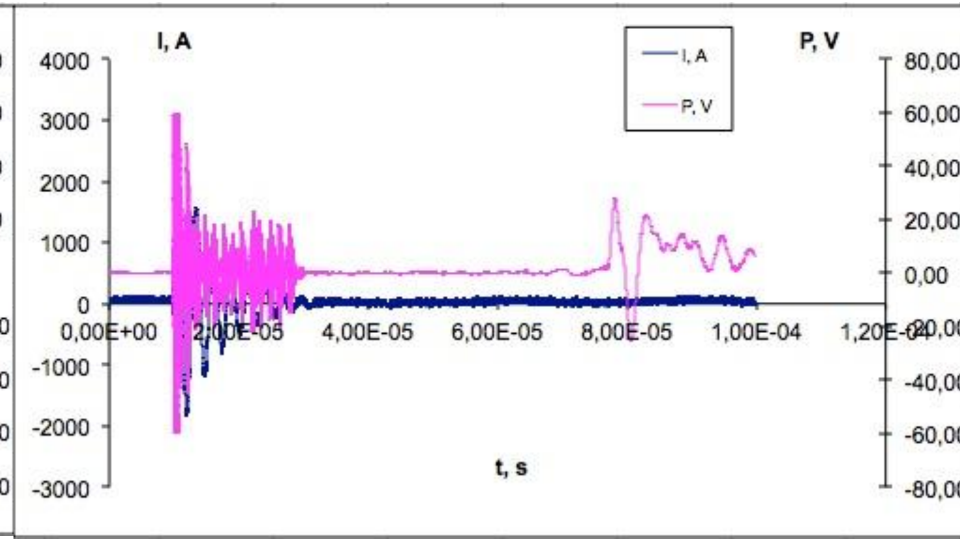




Oscillograms of the discharge current and the acoustic signal
C = 60 nF, U = 19,5 kV, R = 0 Om, Air = 0 cm^3/s, t = 10 mks



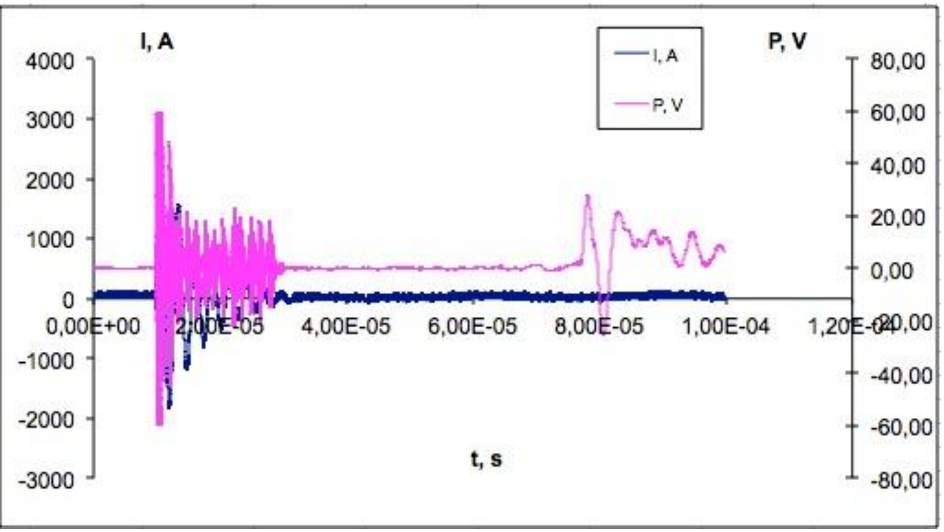
Distillate



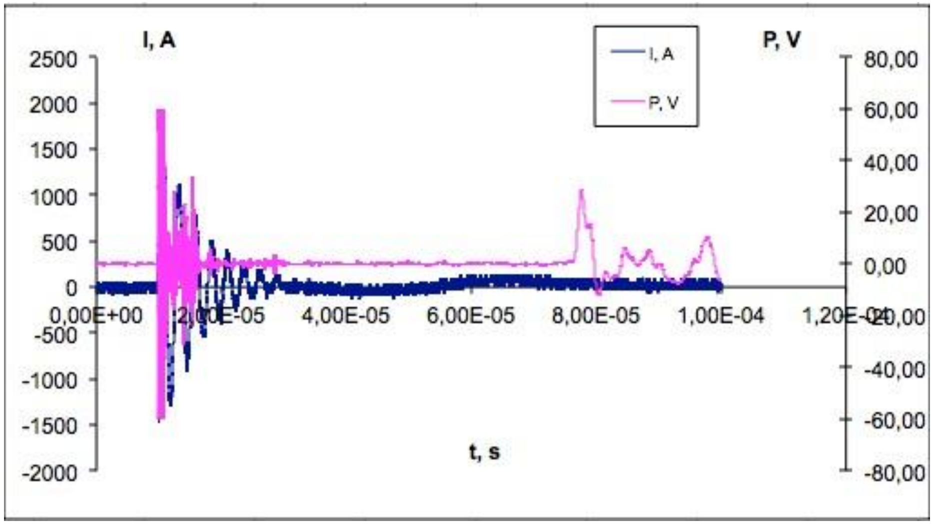
70% Ethanol

At the transition from the distillate to the ethanol solution acoustic signal of the first diverging wave decreases. This may be due to the different densities of liquids.

Oscillograms of the discharge current and the acoustic signal C = 60 nF, U = 19,5 kV, R = 0 Om, t = 10 mks



70% Ethanol, Air = 0 cm³/s



70% Ethanol, Air = 2,5 cm³/s

Without air supply and with air supply acoustic signal varies slightly.

Conclusion

- **In a single pulse mode of the axial discharge current in the cylindrical plasma-liquid system it was found the nonlinear dependence of the ratio of the second diverging wave signal to the amplitude of the first acoustic convergent wave, which generates the previous wave, on the discharge current amplitude.**

- **The pressure of the divergent AW (acoustic wave) grows according to a power law:**

$$P_{aw} = AR^{-\alpha}{}_{aw} \quad , \ \alpha > 1$$

Conclusion

The research of ethanol reforming in pulse PLS has shown that

- **At the transition from the distillate to the ethanol solution acoustic signal of the first diverging wave decreases. This may be due to the different densities of liquids.**

- **Without air supply and with air supply acoustic signal varies slightly.**
- **transition from single pulse mode to double pulse mode is accompanied by reduction syn-gase ratio ([H2]/[CO]).**
- **The energy efficiency of the ethanol reforming is significantly lower in a pulsed mode at low input energies than in the DC mode.**

Thank you for attention!