PLASMA REFORMING OF LIQUID HYDROCARBONS INTO FREE HYDROGEN FOR THE USE IN THE AEROSPACE TECHNOLOGIES

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OUTLINE

Introduction: Features of dynamic plasma-liquid systems with the electrical discharges in the gas channels within the liquids (usual or microporous with microbubbles)

- ***Experimental:*** Plasma-chemical reactors with DC SD, DGCLW, DGCLW US cavitation and plasma-liquid system with the gas-dynamic quenching

Methodology: Research and diagnostics of plasma, gas and liquid phases during the treatment

- ***Basic results***:
  - Properties and parameters of DGCLW plasma;
  - Component content of output syngas products;
  - Efficiency of plasma reforming of liquid fuels
- ***Conclusion***

Introduction

The following two basic tasks should be decided for the creation of hypersonic (M > 5) aircraft:

1. **the presence of quickly combustible fuel on board of aircraft,**
2. **the maintenance of cooling of all aircraft.**

The possible approach to the decision of these tasks can be the board reforming of different hydrocarbon (for example kerosene), i.e. the conversion of hydrocarbon in H_2 and CO_2:

1. **Hydrogen can be used as quickly combustible fuel.**
2. **Dioxide of carbon - for cooling the aircraft.**
3. **The injection of hydrogen rich gas reduces the nitrogen in NO and NO_2 to N_2.**

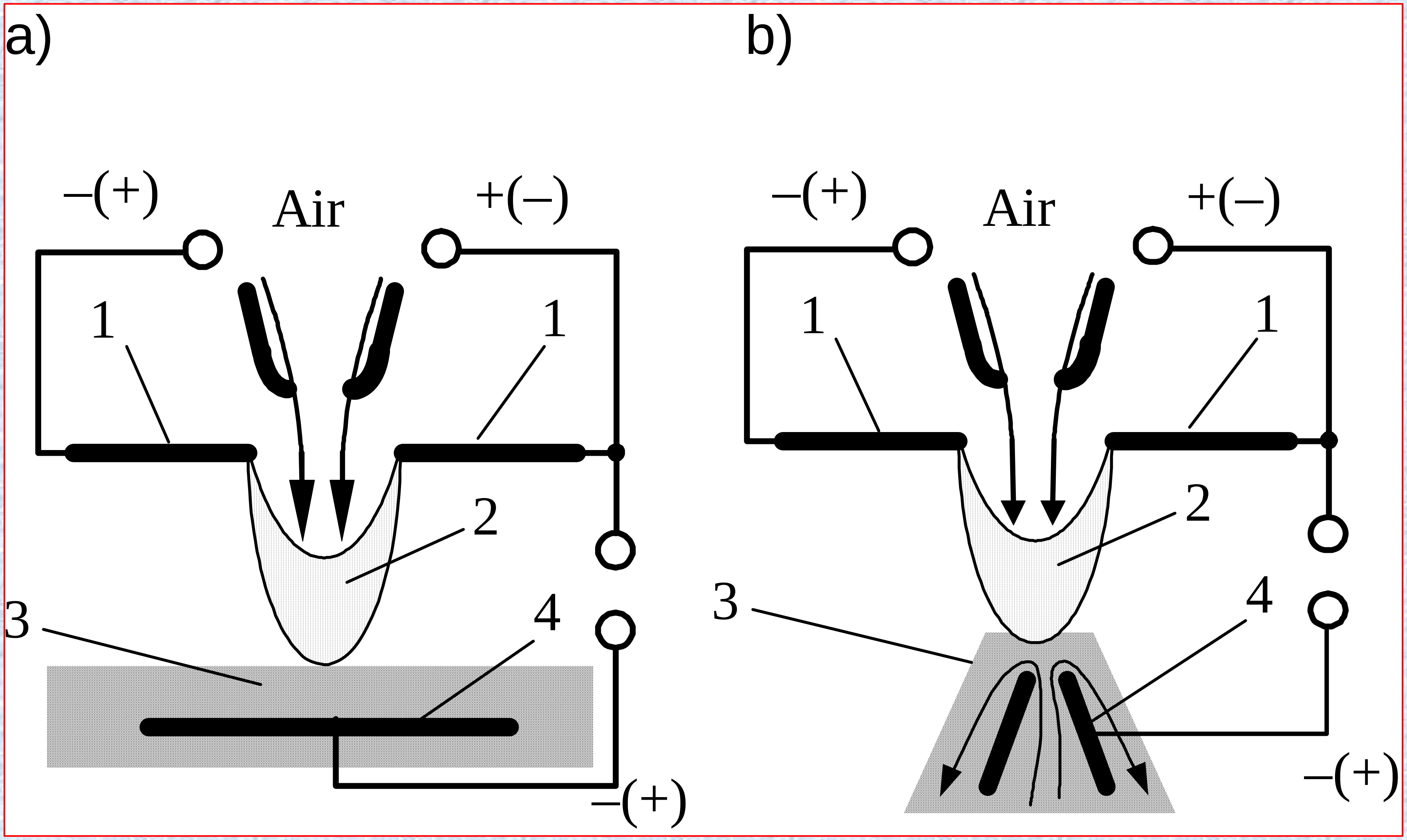
One of the most perspective directions of reforming is plasma assisted pyrolyze of a hydrocarbon and air mix. It is developed as reforming of automobile fuel in syngas (H_2 + CO) [*1*].

This work is related to the novel technology of plasma reforming of liquid hydrocarbon (C_2H_5OH) into hydrogen-enriched synthesis gas (syngas) in dynamic plasma-liquid systems (PLS) using the electrical discharges in the gas channels with liquid wall (DGCLW) [2].

[1] G. Petitpas, J.-D. Rollier, A. Darmon, etc.//Int. J. Hydrogen Energy, vol. 32, pp. 2848-2867, 2007.

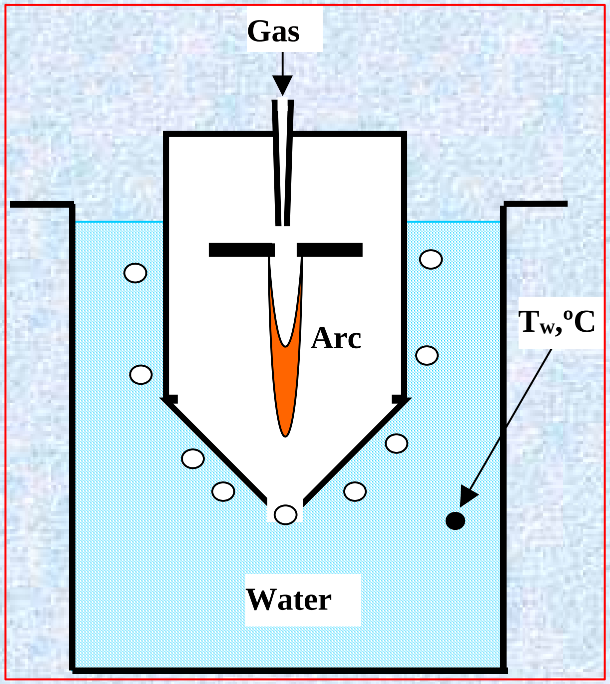
[2] V.Ya. Chernyak, S.V. Olszewski, V.V. Yukhymenko, etc. //IEEE Trans. Plasma Sci., 36(6) 2933-2939 (2008)

Principal schemes of experemental set-up with the secondary discharges of static and dynamic types in usual liquid



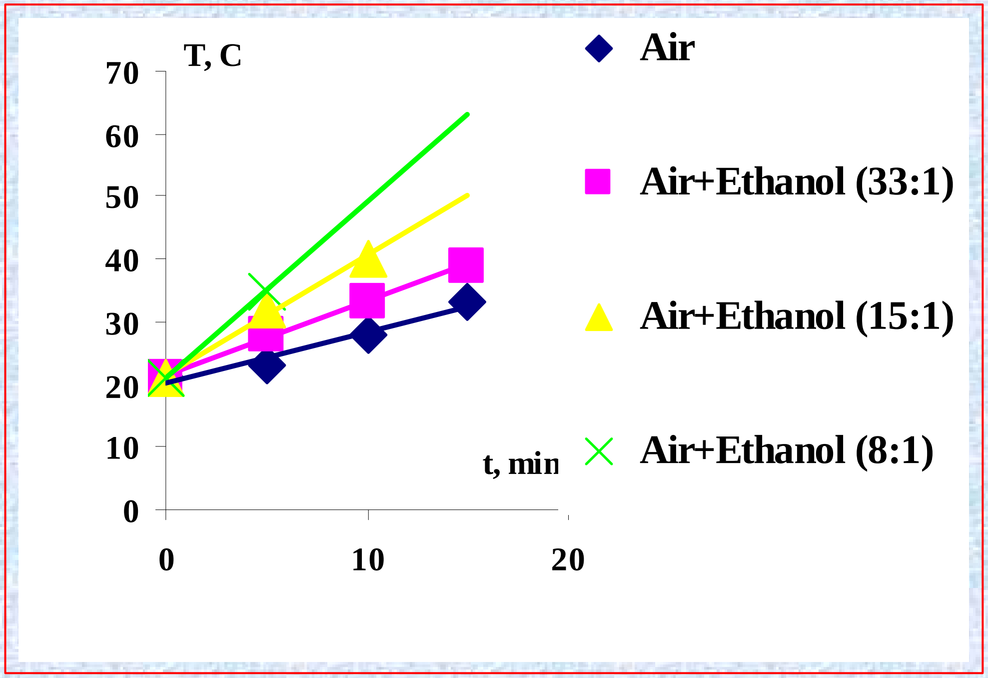
Calorimetry of fuel-air mixture with the blowing transverse arc

a)



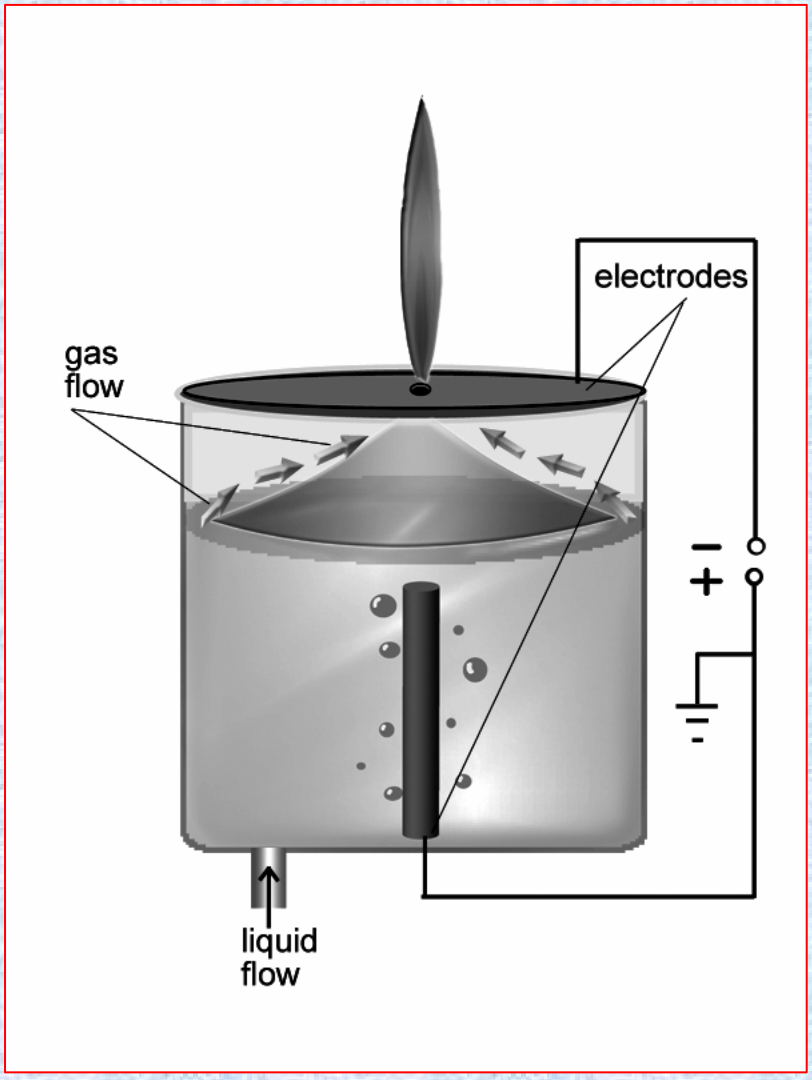
Calorimeter scheme

b)

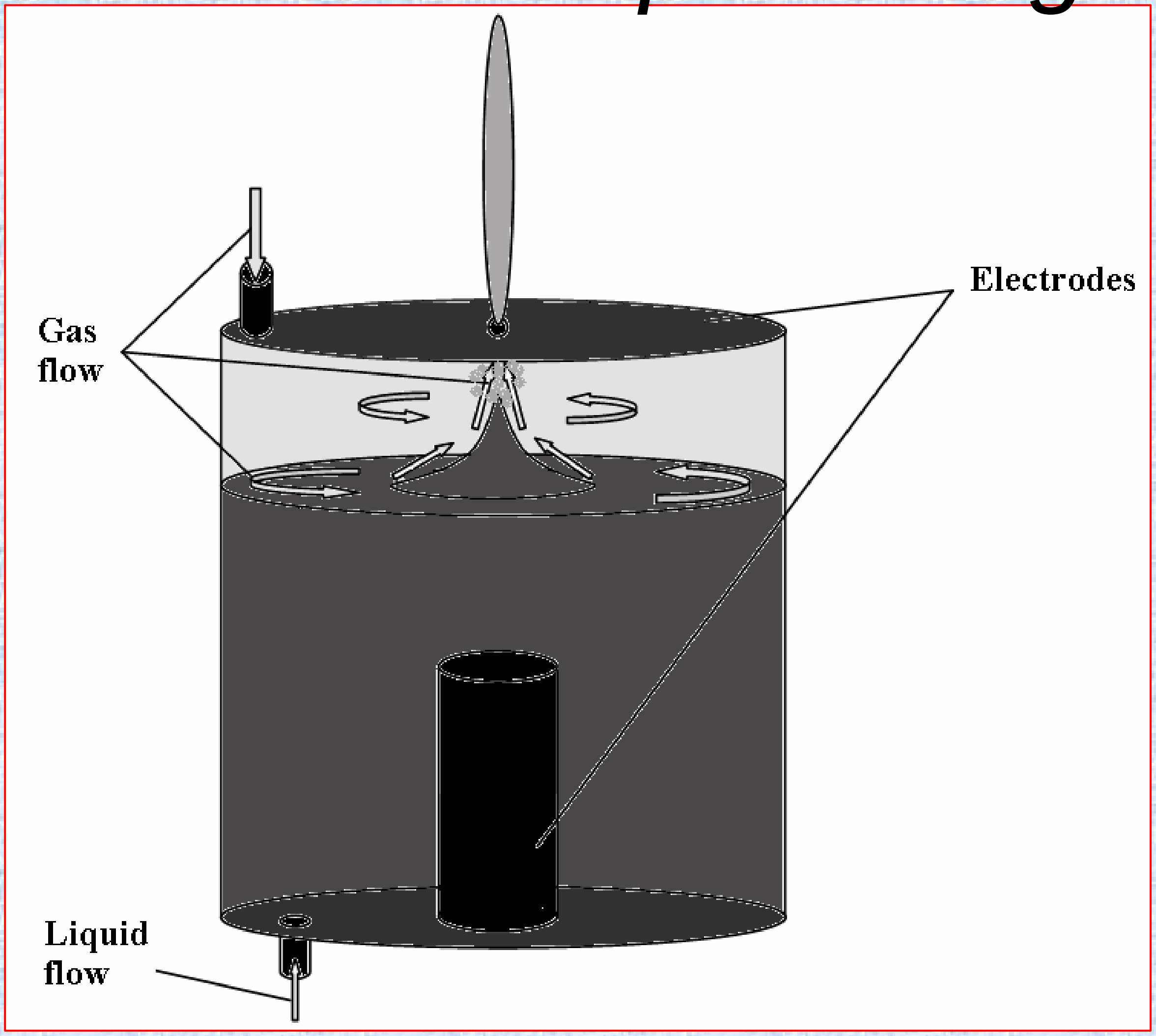


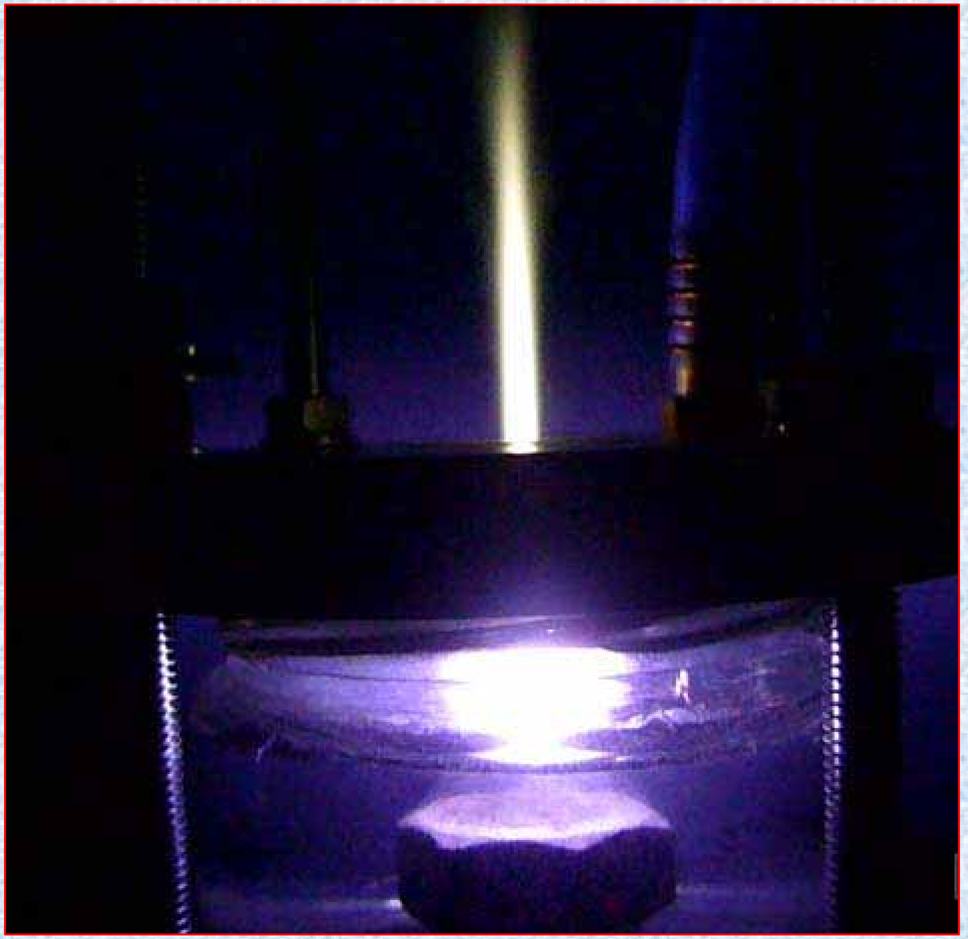
Dependences of water temperature in a calorimeter from the arc burning time

Plasma-liquid system with the gas-dynamic quenching

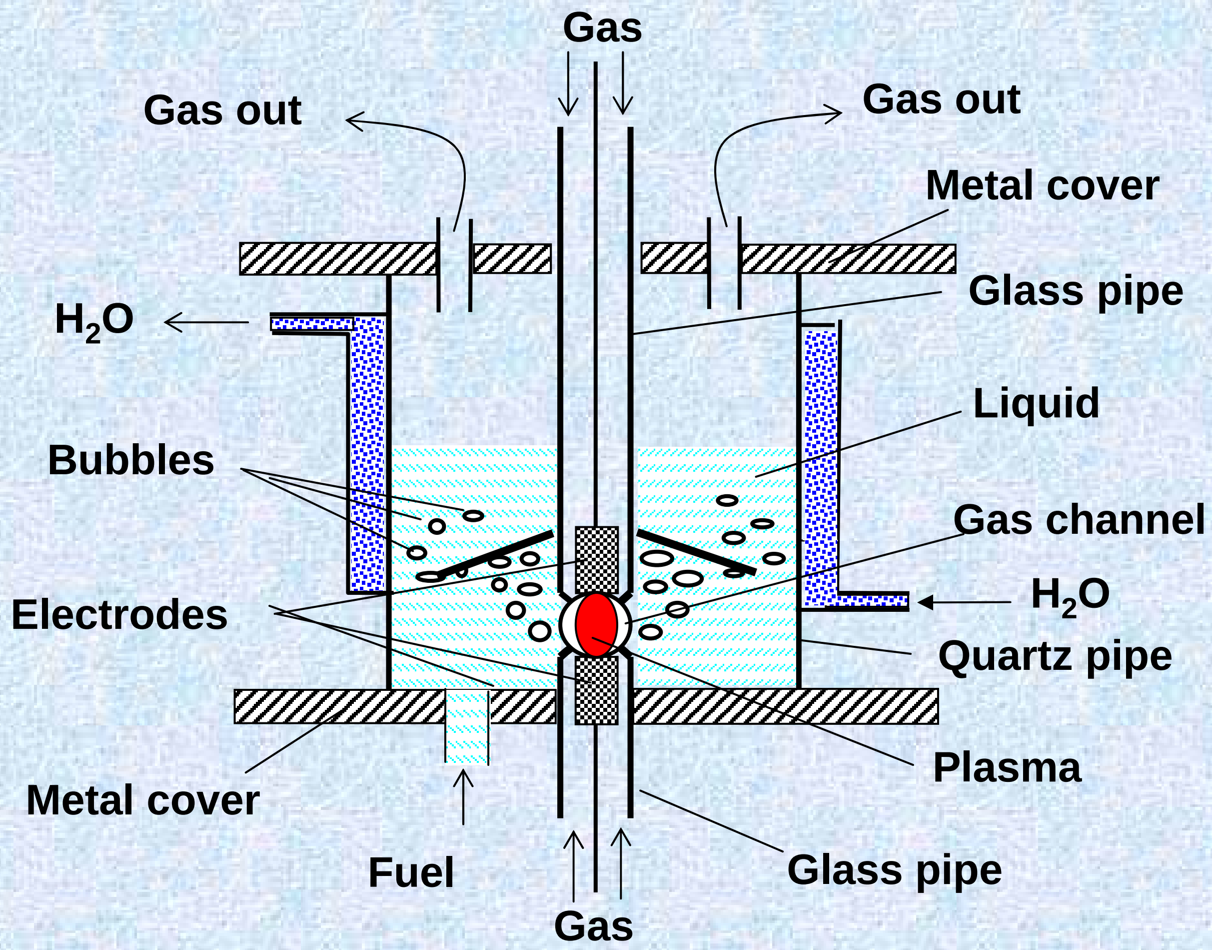


Plasma-liquid system with reverse vortex flow and quenching



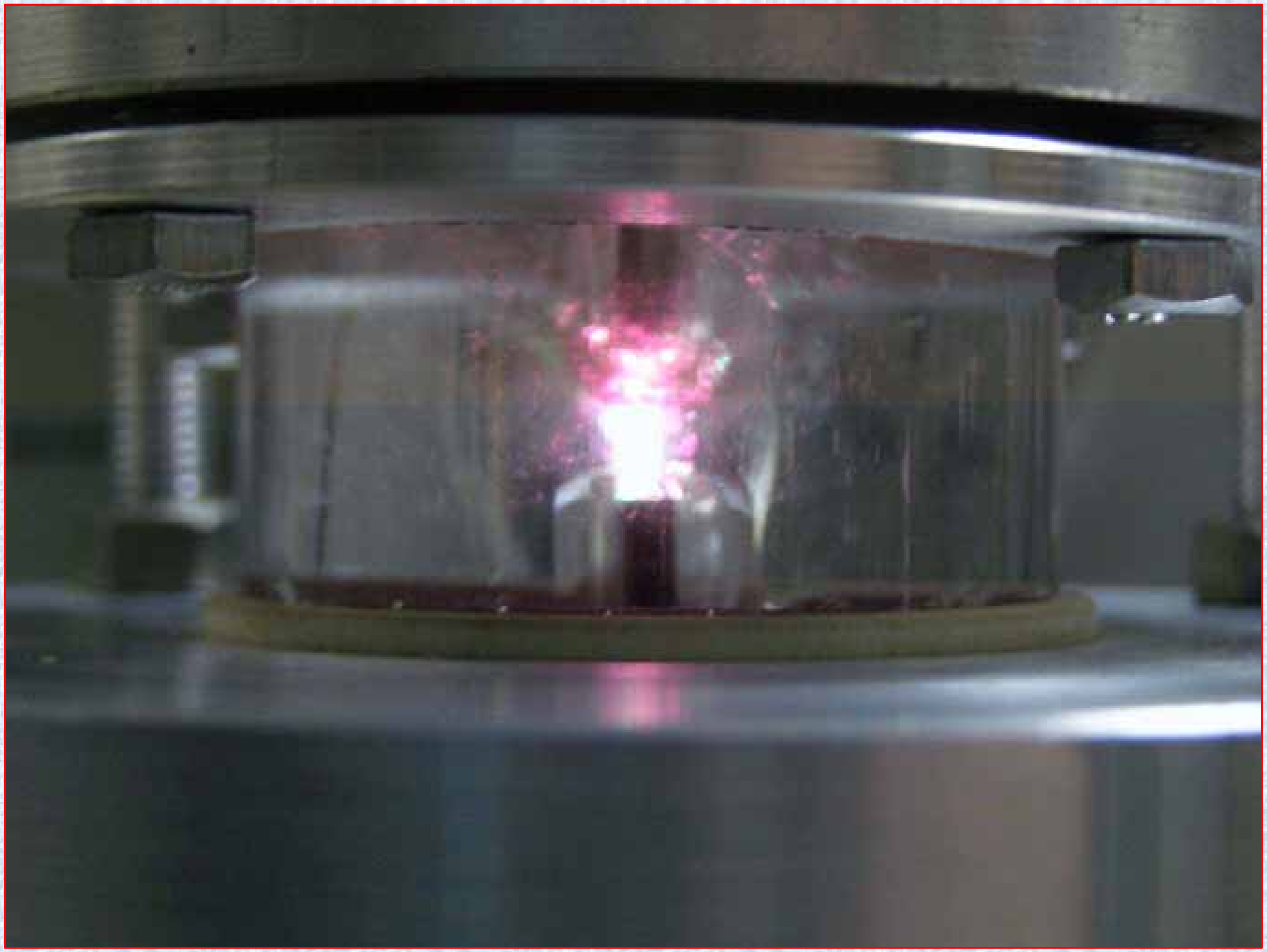


Plasma-chemical reactor with DGCLW

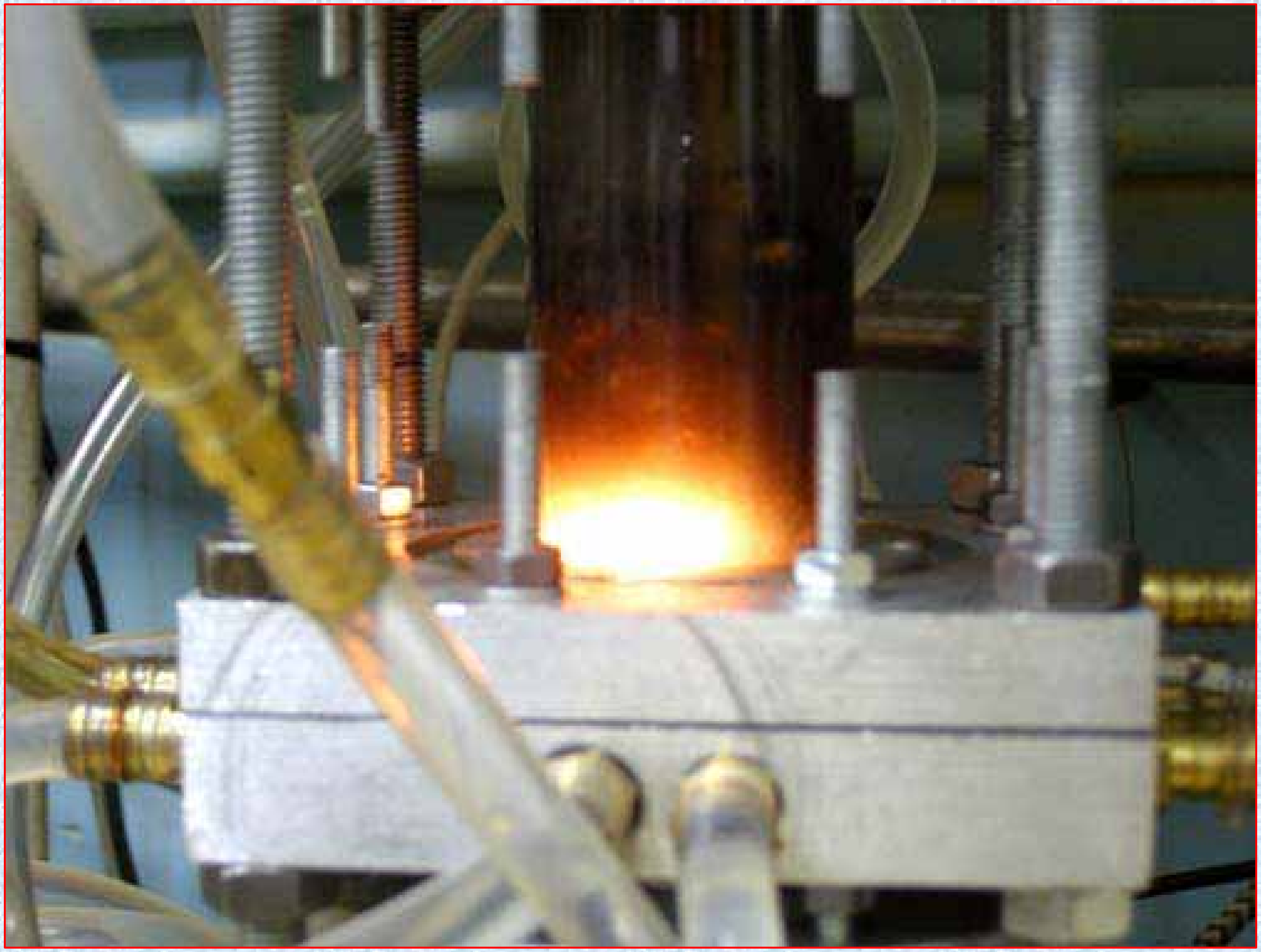


Electrode system of DGCLW

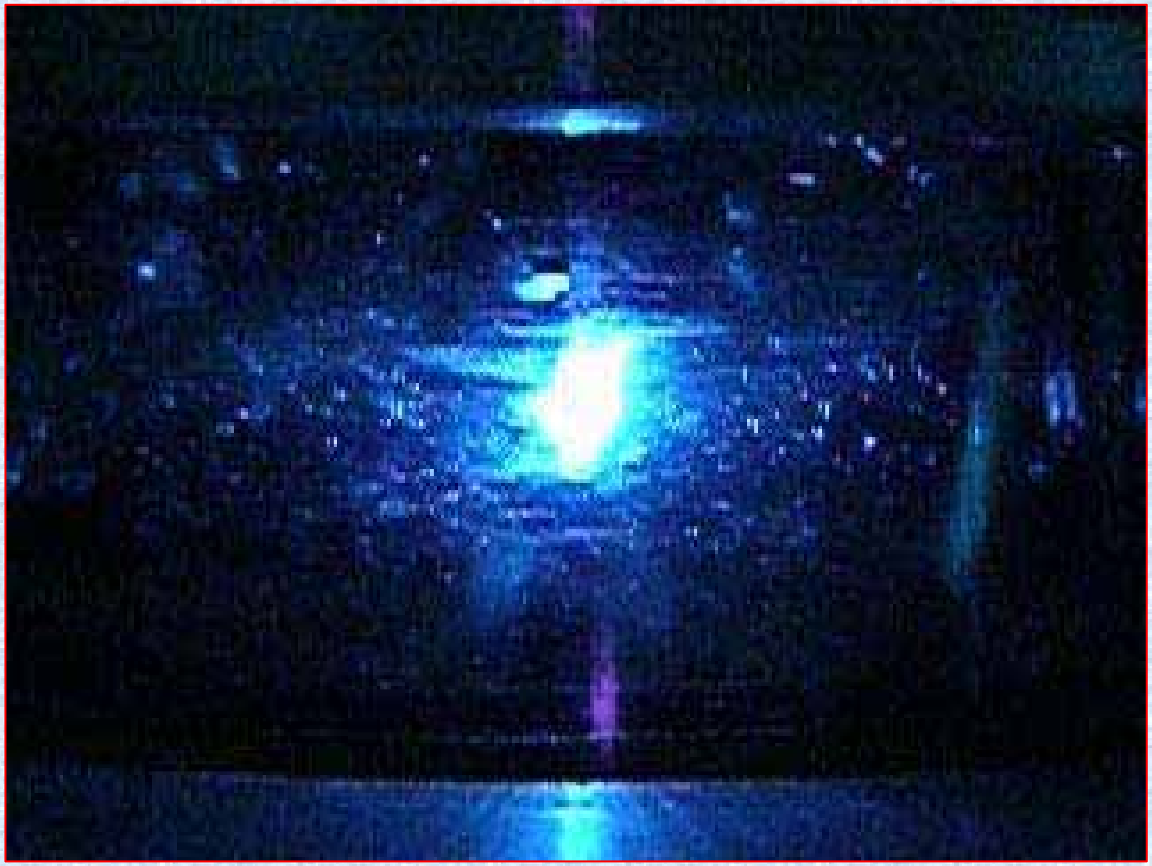
DGCLW work at constant air flow in water



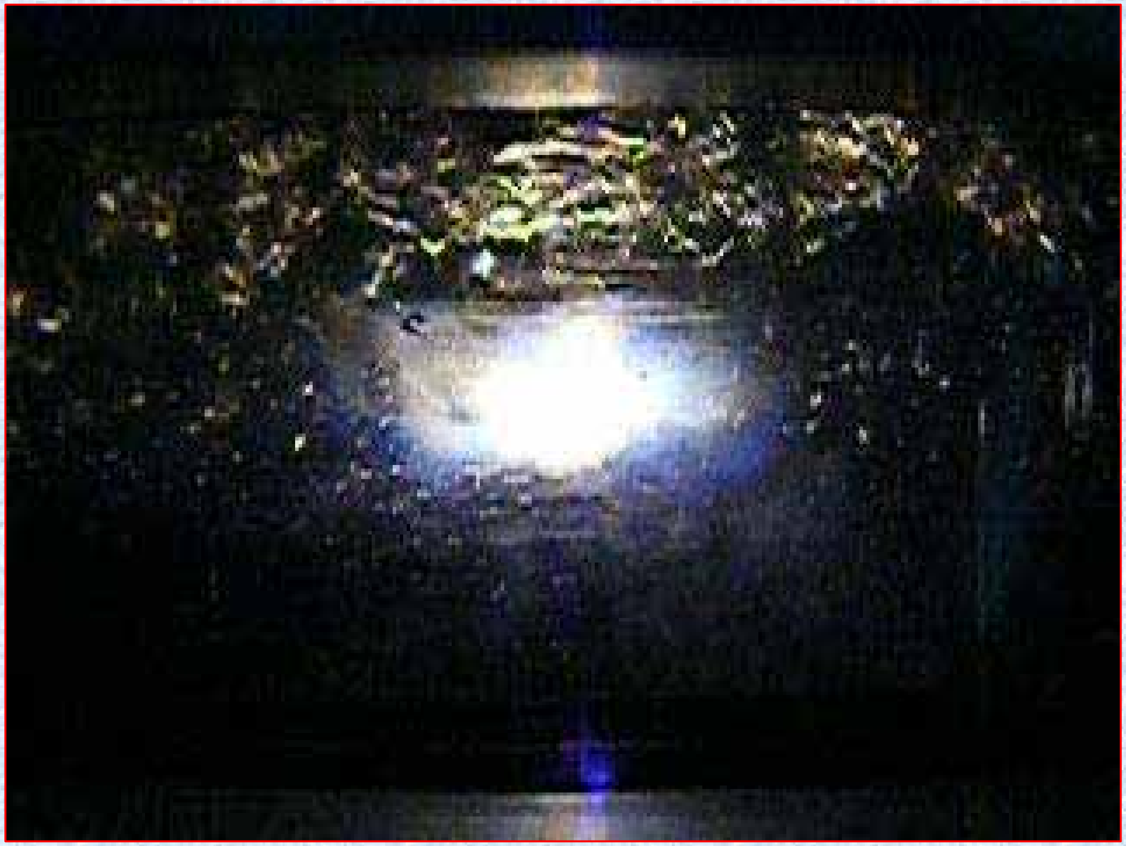
DGCLW work at constant air flow in diesel fuel



DGCLW work with two solid electrodes at constant air flow (G_{air} = 55 cm^3/s, I = 200 mA)



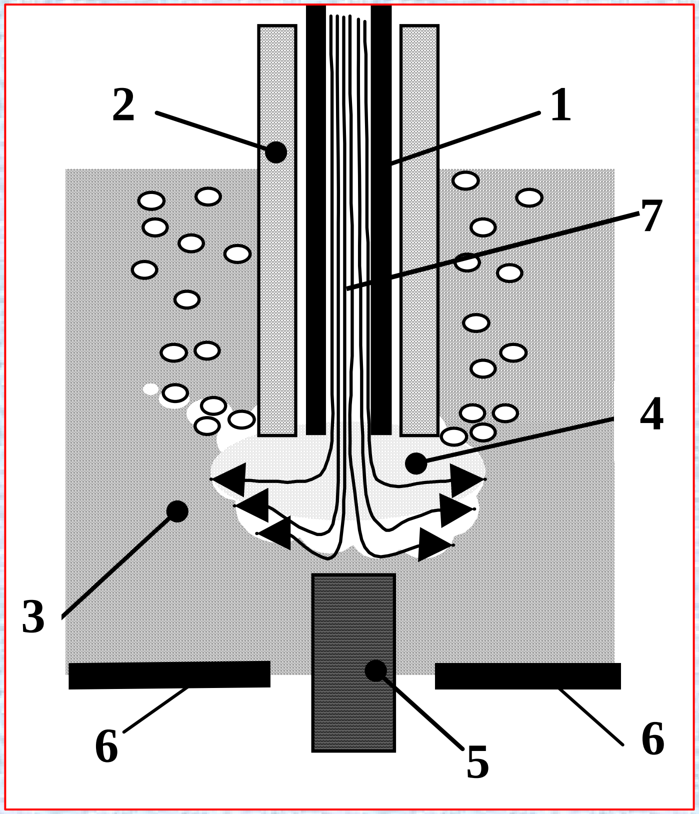
DGCLW work with “liquid” anode at constant air flow (G = 55 cm^3/s, I = 200 mA)



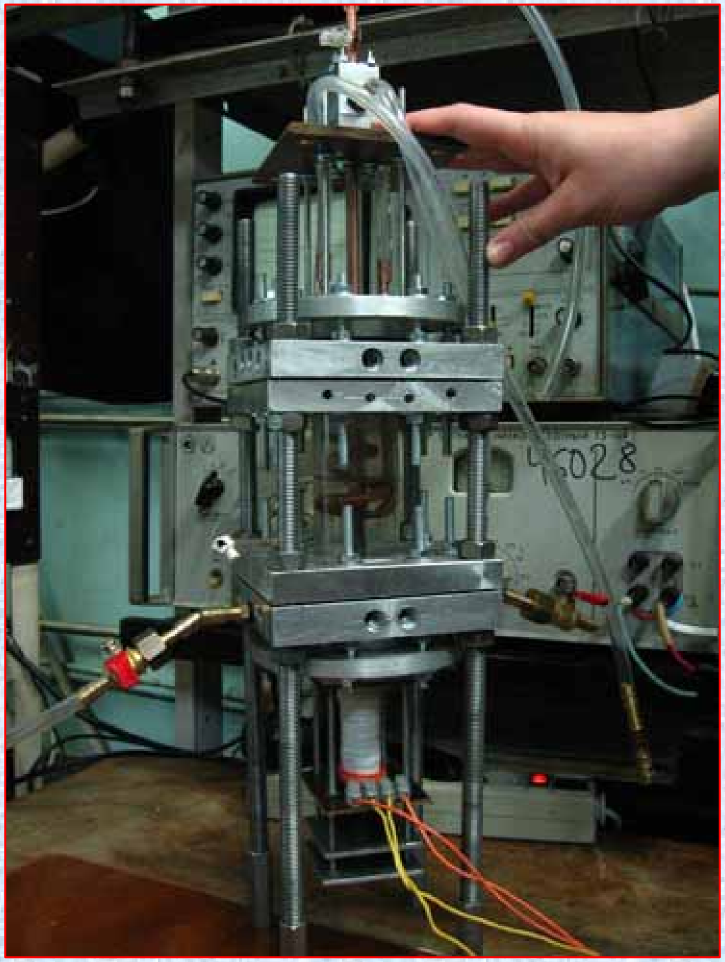
DGCLW work with “liquid” cathode at constant air flow (G = 55 cm^3/s, I = 200 mA)

Plasma-chemical reactor

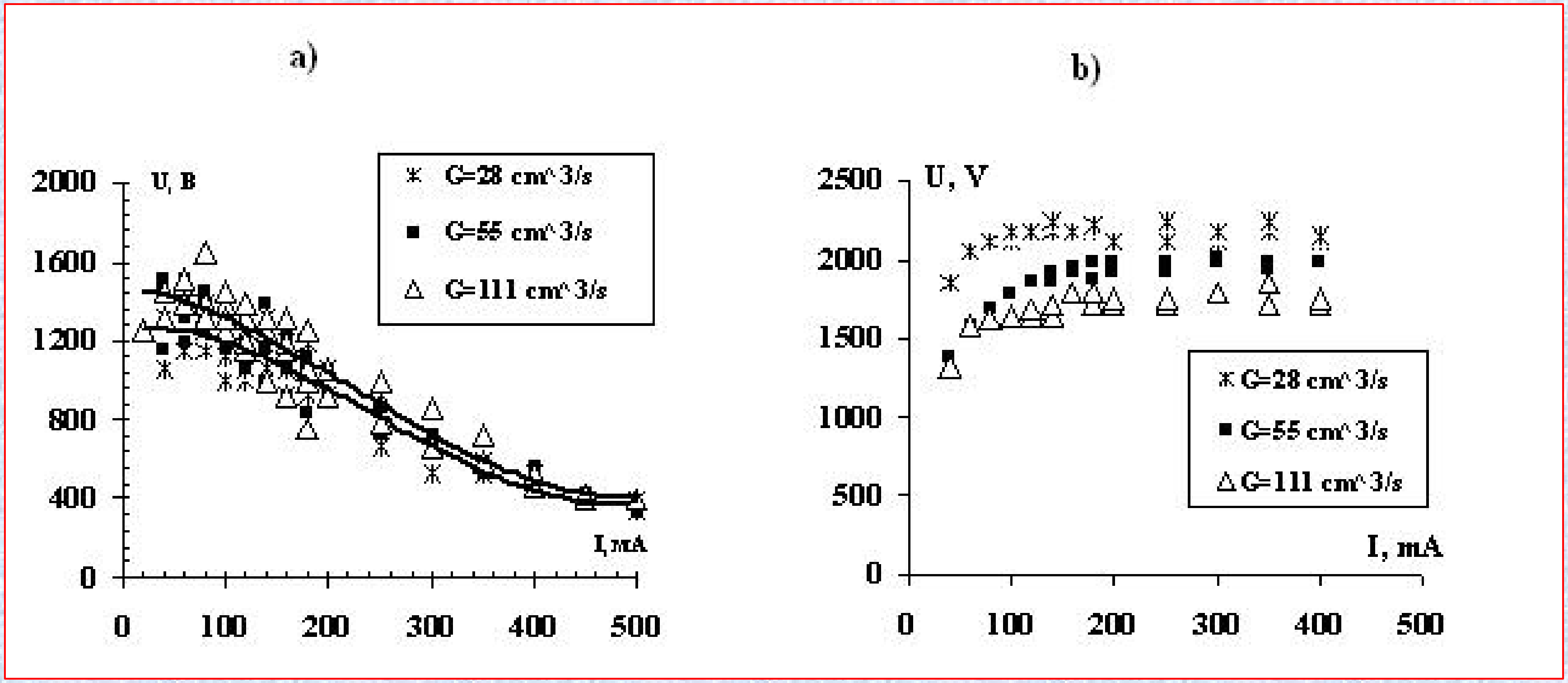
with magnetostrictive transmitter



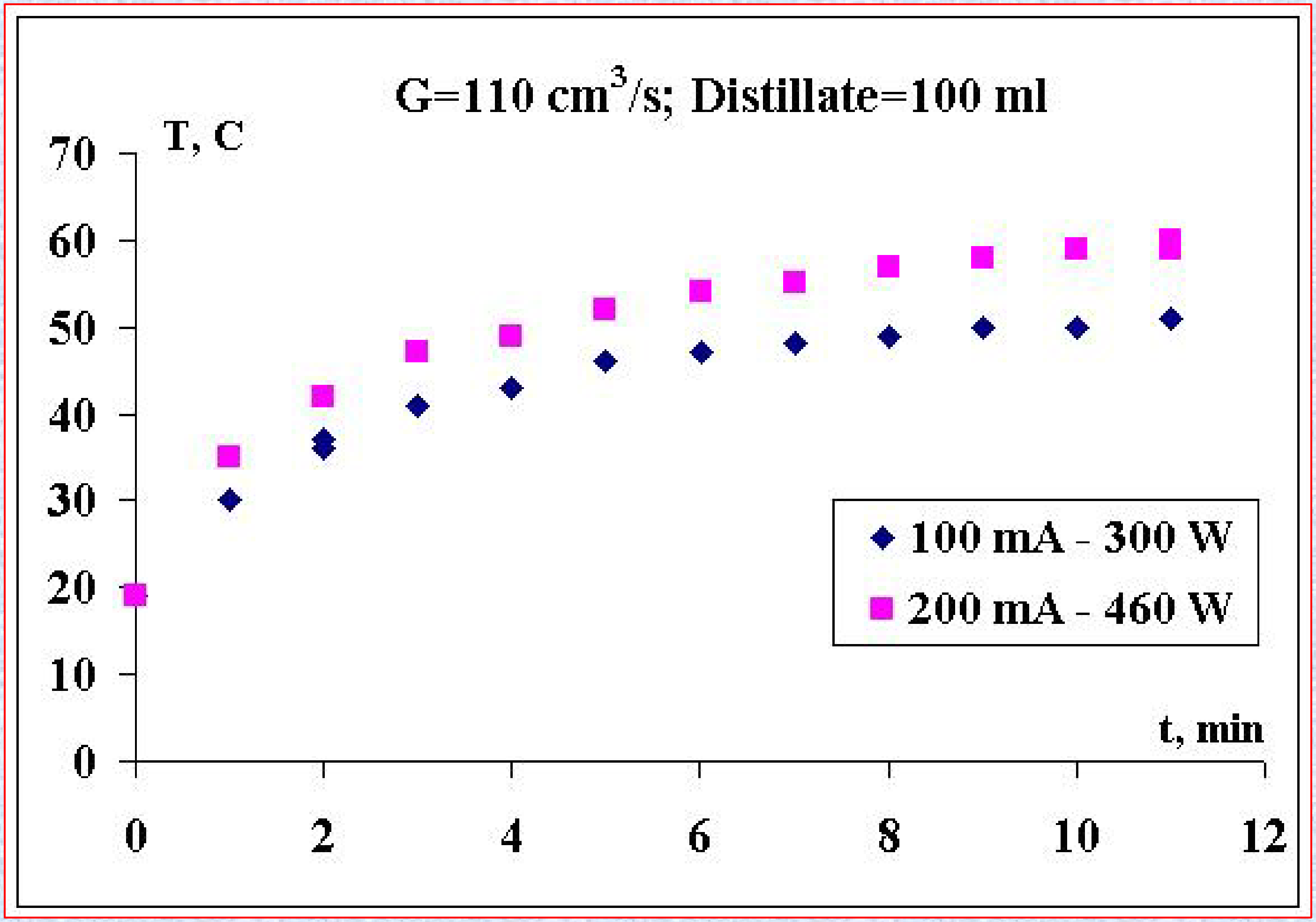
1-metal pipe (electrode), 2 - dielectrical pipe, 3 - liquid, 4 - plasma, 5 - US magnetostrictive transmitter, 6 - metal flange (electrode), 7 - gas flow.



Current-voltage characteristics of the DGCLW in ethanol water (1/ 5) solution :
a – mode with solid electrodes;
b – mode with "liquid" cathode



Temperature conditions in the liquid during the DGCLW operation



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Experimental methods

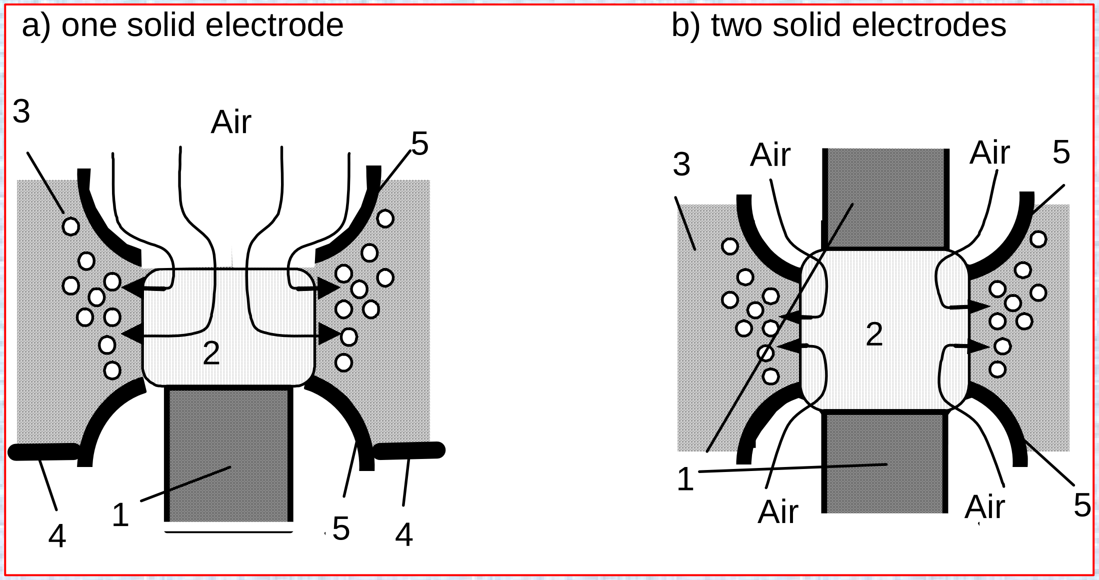
For DGCLW plasma – optical emission spectroscopy:

- **SPECAIR code [*http://www.specair-radiation.net*] for determination of different temperatures (electronic, vibrational, rotational)** ***[Z. Machala, M. Janda, K. Hensel, et al: J. Mol. Spectr. 243, p. 194 (2007).],***
- **SPECAIR code for determination of concentration of neutral and ionic components (*N, O, C, NO, N2, N2+, OH, NH, C2, CN, CO*) [*Prysiazhnevych I.V., Chernyak V.Ya., Olszewski S.V., Yukhymenko V.V. // Chem. Listy 102, s1403−s1407 (2008)]***

For basic components of output syngas products (H_2 , CO, CH_4, C_2H_2, C_2H_4, and C_2H_6):

- **gas-chromatography ,**
- **mass-spectrometry.**

Numerical modelling of DGCLW-PLS (physical model):



1 - electrode, 2 - plasma, 3 - liquid, 4 - metallic flange, 5 - glass pipe

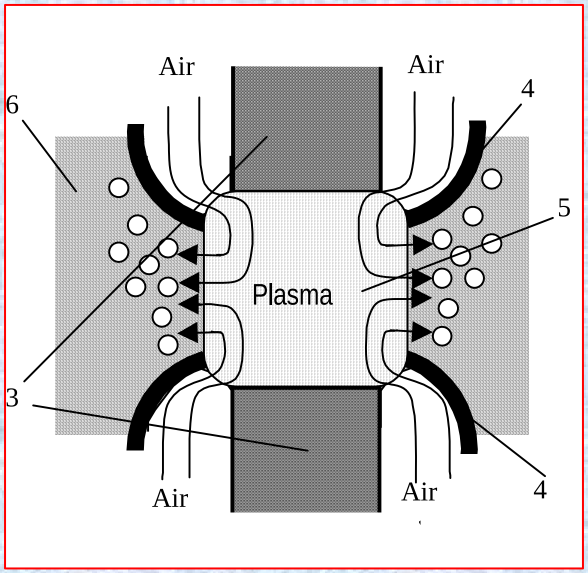
It is assumed that

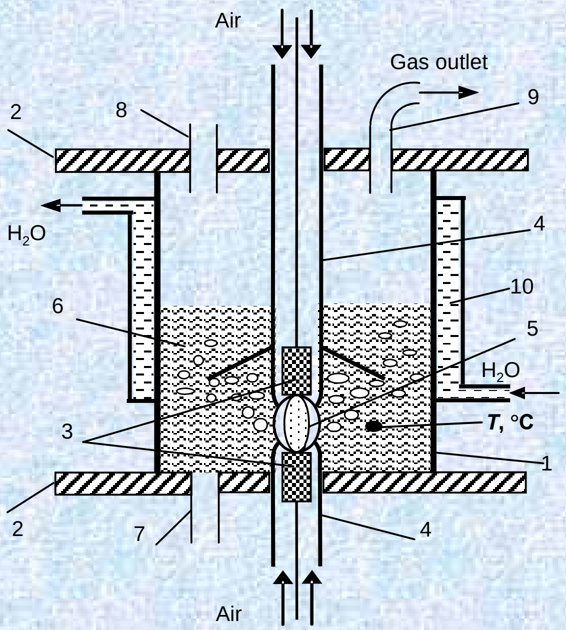
- **electric power introduced into the discharge is immediately averaged in the discharge volume;**
- **internal electric field in the discharge does not vary in space and time;**
- **during the pass of air through the discharge into the reactor volume its content is totally refreshed and its flow rate in the reactor volume is the same as in the discharge gap.**

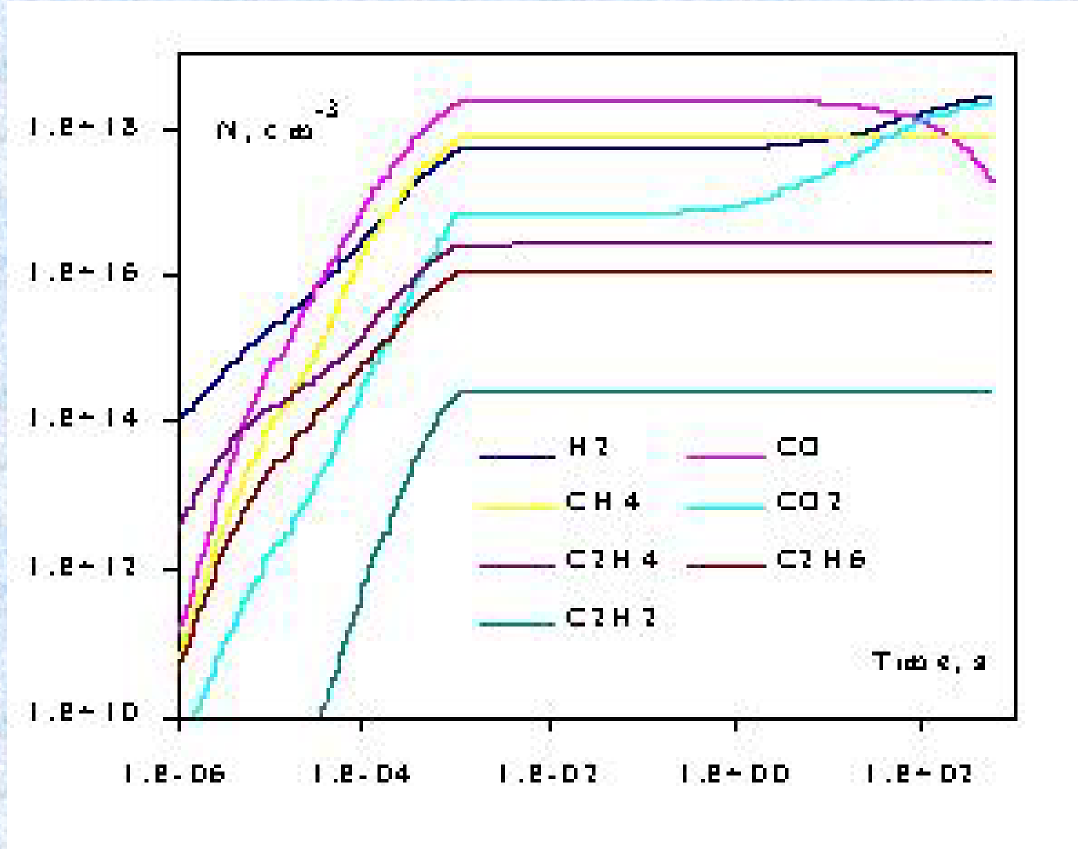
Numerical modelling of DGCLW-PLS (mathematical model):

- **Boltzmann equation for electron energy distribution function and 1D fluid (volume averaged) model [A. I. Shchedrin, D.S. Levko, V.Ya. Chernyak, V.V.Yukhymenko, V.V. Naumov, *JETP Letters*, 88 (2) 107-110 (2008)]**
- **Set of plasma-chemical kinetic equations for kinetically valuable components of air-ethanol-water plasma system. The full kinetic mechanism includes 59 components (C_2H_5OH, N_2, O_2, H_2O, H_2, CO, etc), 76 electron-molecular processes, and 364 chemical reactions (details available at Web-site http://www.iop.kiev.ua/~plasmachemgroup)**
- **Cross sections and rate constants for plasma-chemical reactions in air-ethanol-water system according to NIST recommendations [NIST Scientific and Technical Databases Online. Available: http://www.nist.gov/srd/]**

Plasma reforming of ethanol in DGCLW-PLS

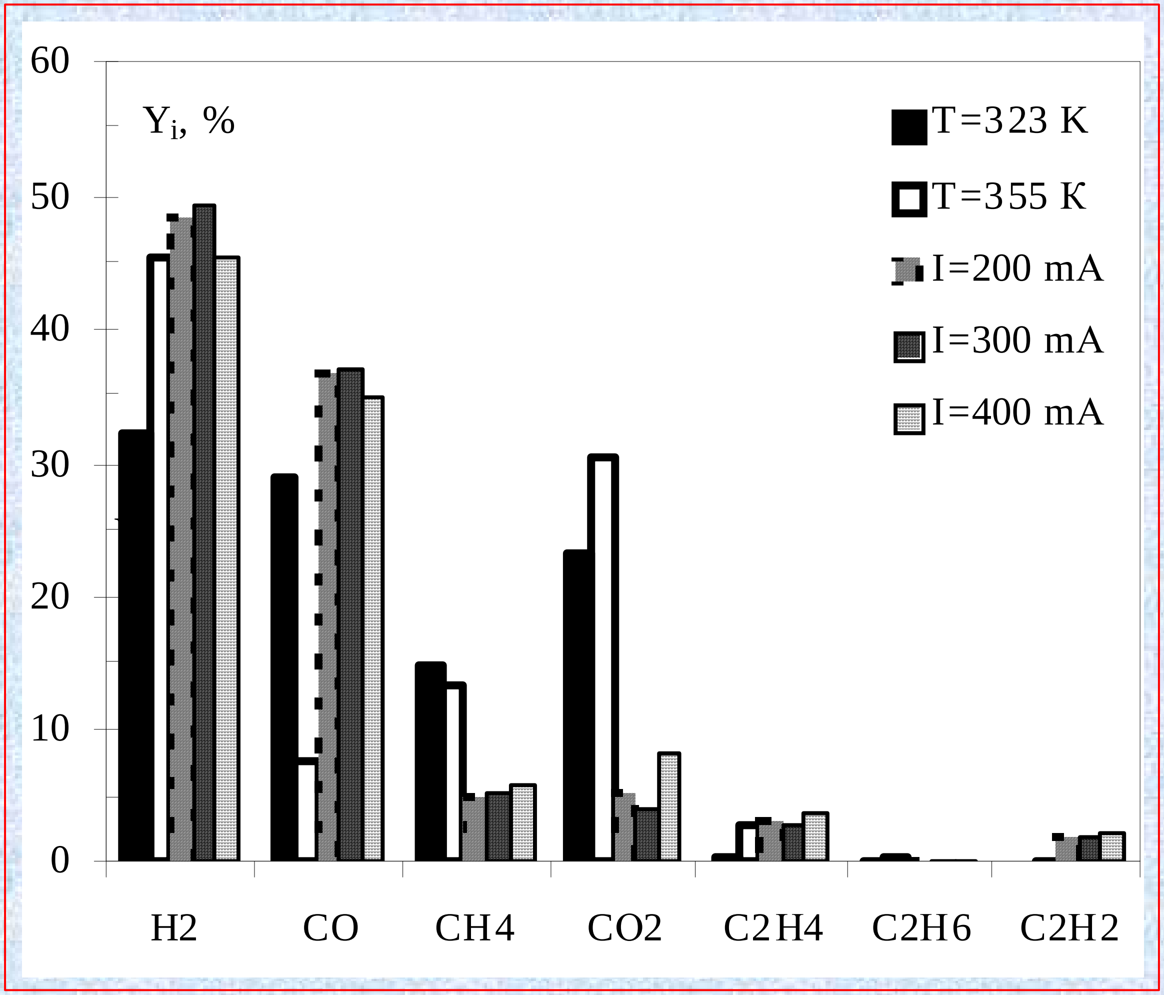






Calculated time dependences of concentrations of the main gas components during the processing in the DGCLW discharge and in the PLS reactor at temperature conditions *T*= 323 K

Component content of output gas products after the ethanol conversion in DGCLW-PLS at measurements and calculations



Controlled parameters of ethanol reforming in PLS-DGCLW

α - coefficient of energy transformation

$$\alpha = \frac{\sum_i Y_i \times LHV(Y_i)}{IPE}$$

***Y_i* – molar fraction,**
***IPE* - the input plasma energy,**
***LHV* - the lower heating value,**
HC – the injection hydrocarbon fuel

η - efficiency from Petitpas ***[G. Petitpas, J.-D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, and L. Fulcheri //Int. J. Hydrogen Energy, vol. 32, pp. 2848-2867, 2007]***

$$\eta = \frac{(Y_{H_2} + Y_{CO}) \times LHV(H_2)}{IPE + Y_{HC} \times LHV(HC)}$$

Controlled parameters of ethanol reforming in PLS-DGCLW

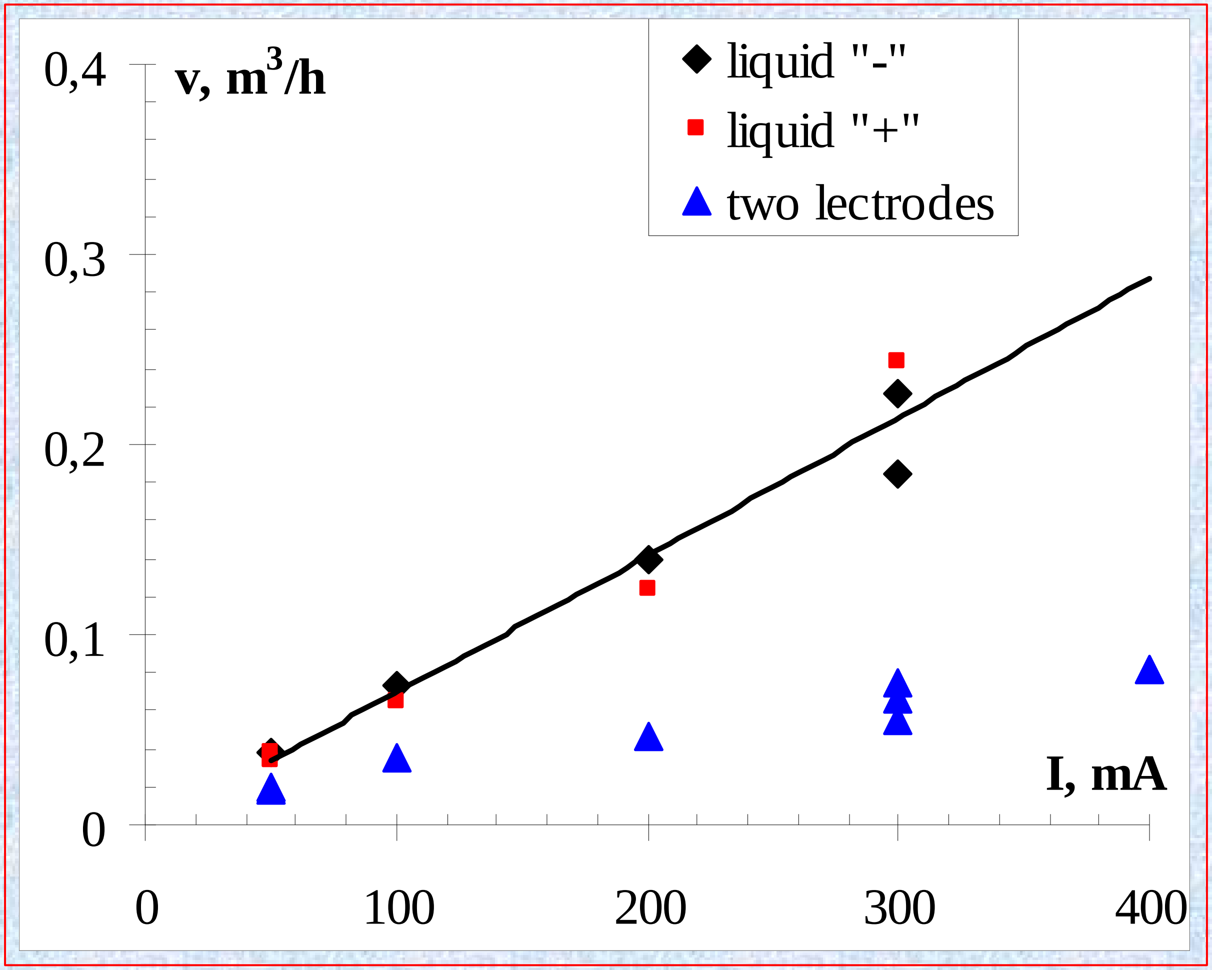
Specific energy requirement - ν

[*G. Petitpas, J.-D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, and L. Fulcheri, "A comparative study of non-thermal plasma assisted reforming technologies", Int. J. Hydrogen Energy, vol. 32, pp. 2848-2867, 2007*].

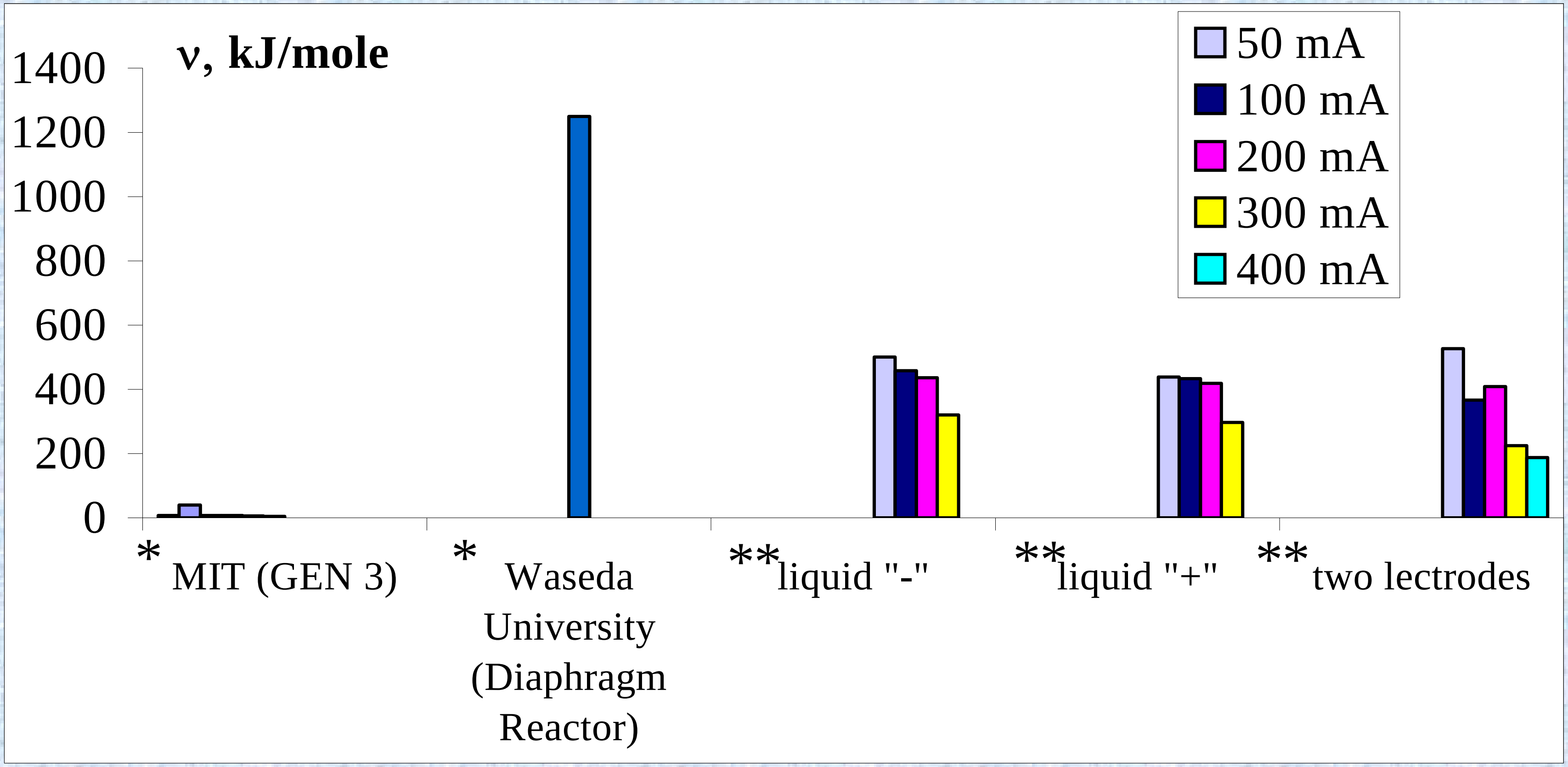
This value is the input electrical power used by the plasma that is required for producing one mol of H2. Still considering the CO produced, the specific energy requirement is:

$$\nu = \frac{Input\_Plasma\_Power}{(H_2 + CO)_{produced}}$$

Generation rate of synthesis gas at the process of ethanol reforming in PLS-DGCLW. $G_{air} = 55\ cm^3/s$



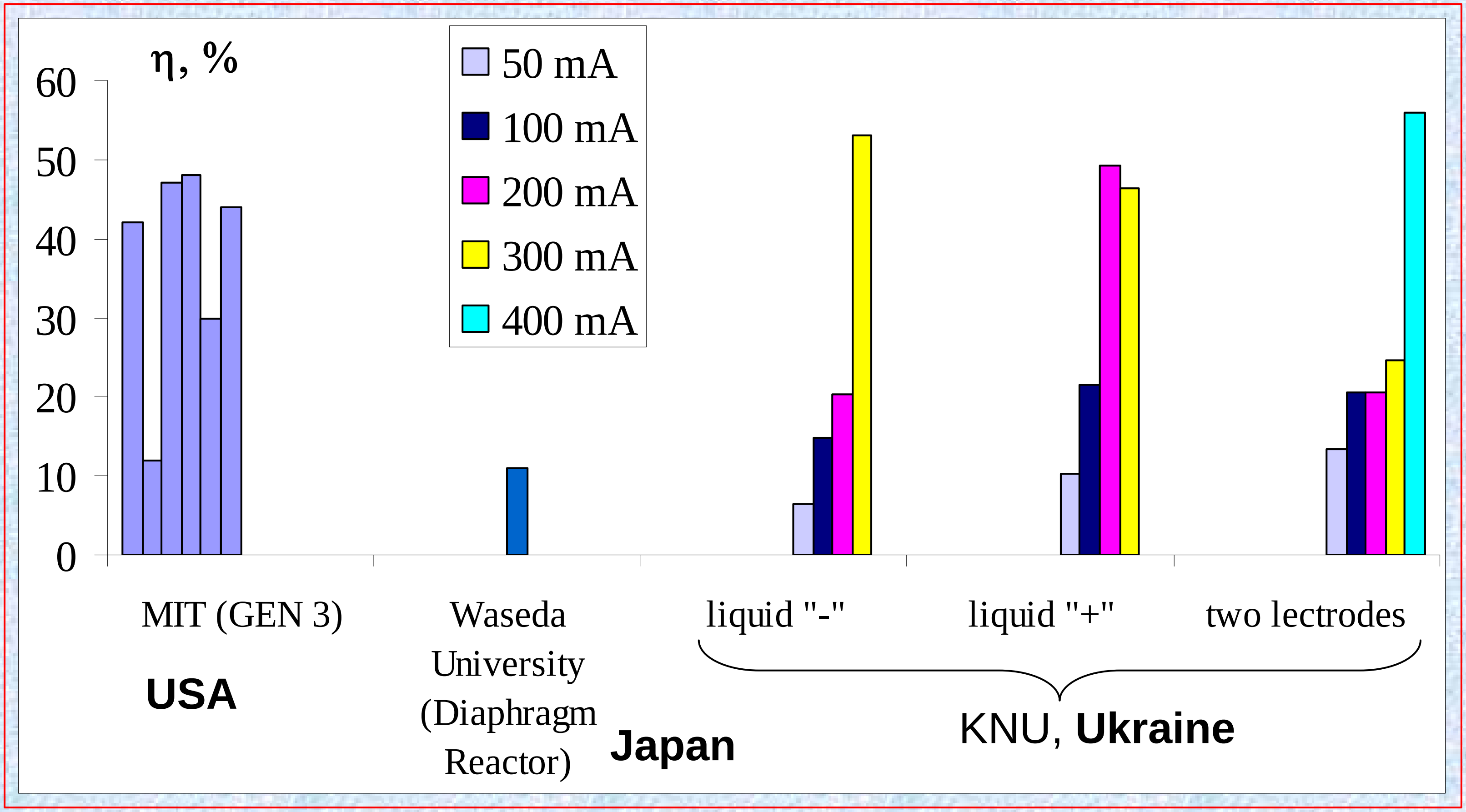
Specific energy requirement of non-thermal plasma processes



* G. Petitpas, J.-D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, and L. Fulcheri, "A comparative study of non-thermal plasma assisted reforming technologies", *Int. J. Hydrogen Energy*, vol. 32, pp. 2848-2867, 2007.

** This work

Efficiency of non-thermal plasma processes



Conclusions

- **The dynamic plasma-liquid systems with the electric discharges in the gas channels with liquid wall is quite efficient in plasma-chemical reforming of ethanol into free hydrogen and synthesis gas.**

- **The minimal value of power inputs in investigated discharge modes is ~2.4 kWh/m^3 at the power of output syngas of ~4.4 kWh/m^3.**

- **The electric discharge in gas channel with liquid wall have high power efficiency and efficiency of the non-equilibrium plasma processes comparable to other known gas-discharge plasma sources of the atmospheric pressure such as diaphragm and arc types.**

The main purpose of R&D activities in KNU on problems of non-thermal low-temperature plasma-assisted bio-fuel reforming are process research + performance study + fuel property testing + recommendations.

The main advantages of use of plasma-assisted reforming of alternative bio-fuels for applications in aviation

- **physical & chemistry aspects: improving characteristics of synthetic hydrogen-enriched fuel ignition and combustion in aircraft jet engines,**

- **environmental ecology & climate aspects: reducing pollution emission of NOx, COx, SOx, soot, etc in atmospheric air,**

- **economic aspects: usage of alternative renewable (derived from agricultural biomass) bio-fuels instead of fossil oil petroleum-dependent hydrocarbon fuels in commercial aircrafts.**

Acknowledgments

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Thank you for attention