Bioethanol and bioglycerol conversion in "tornado" type plasma–liquid system with the addition of CO2

V.Ya. Chernyak[1], O.A. Nedybaliuk[1], Ol.V. Solomenko[1], E.V. Martysh[1], V.A. Andryushenko, T.E. Lisitchenko[1], L.V. Simonchik[2], V.I. Arkhipenko[2], A.A. Kirillov[2], A.I. Liptuga[3]

[1]Taras Shevchenko National University, Faculty of Radio Physics, Prospect Acad. Glushkova 4G, Kyiv, 03022, Ukraine

[2]B.I. Stepanov Institute of Physics, National Academy of Sciences, Minsk, Belorusssia

[3]V.E. Lashkaryov Institute of Semiconductor Physics, National Academy of Science of Ukraine, Prospect Nauki 41, Kyiv, 03028, Ukraine

chernyak_v@ukr.net

Motivation:

- The generation of plasma requires consumption of the most expensive type of energy - electrical energy.
- The plasma as a source of various active particles can be the good catalyst for chemistry.
- The embedding plasma-chemical technologies in traditional chemical should result in increase of energy efficiency of plasma-chemistry.
- Embedding of plasma-chemical technologies in traditional chemical for increase of controllability last.
- Known that the addition of CO_2 in the plasma-liquid system by reforming hydrocarbons can help to control the plasma-chemical processes (ratio of H_2 to CO)

Methodology:

Plasma was studied using the method of emission spectroscopy:

- ❖ Bolcman plots
- ❖ SPECAIR code [http://www.specair-radiation.net]

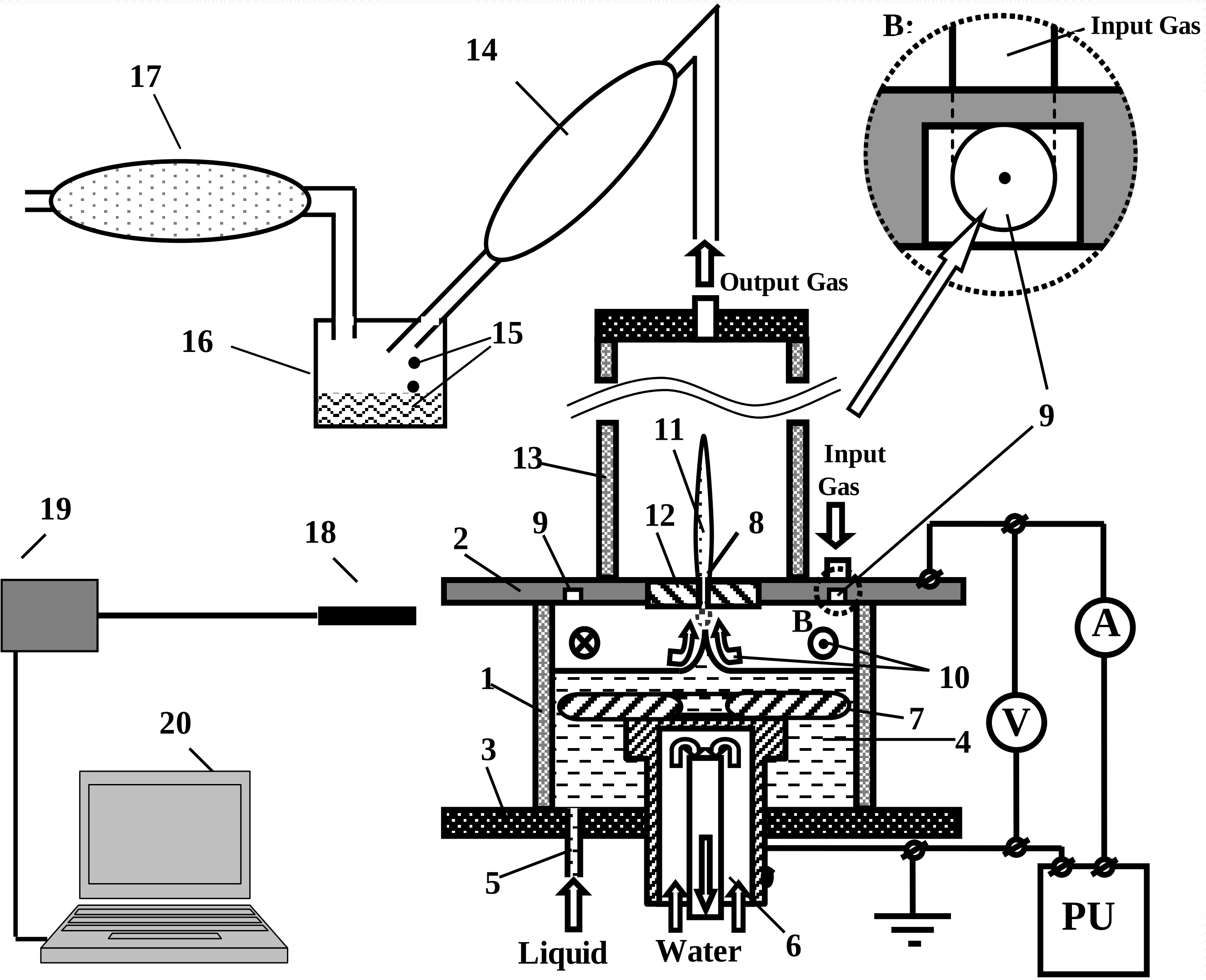
For research of gas products at the outlet of the system where used

- ❖ gas chromatography,
- ❖ mass-spectrometry,
- ❖ infrared spectrophotometry (*IRS*).

Experimental:

DC discharge in a reverse vortex gas flow of tornado type with a "liquid" electrode - TORNADO-LE

[Chernyak V.Y. at all //Patent of Ukraine for useful model № 72913.-2012. - 12.]



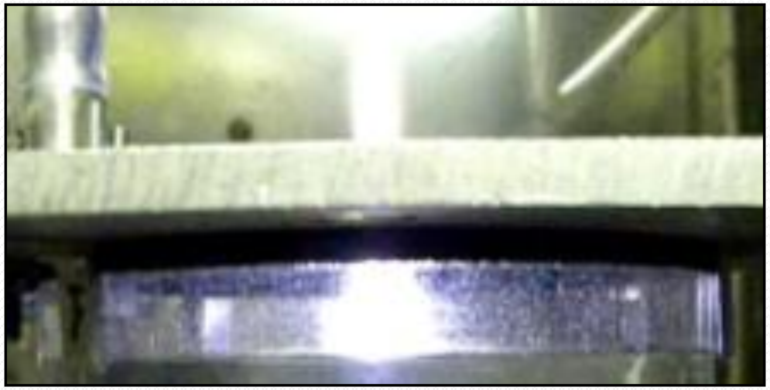
1 – cylindrical quartz vessel;
2, 3 – top and bottom flange;
4 – working liquid;
5 – inlet pipe;
6 – electrode;
8 – axial nozzle;
9 – entrance hole;
10 – rotating gas;
11 – jet;
7, 12 – stainless steel and copper hub;
13 – quartz chamber;
14, 15, 16 – water cooling;
17 – flask;
18 – optical fiber,
19 – spectrometer;
20 – computer.

Experimental: Photo of experimental setup

Liquid cone

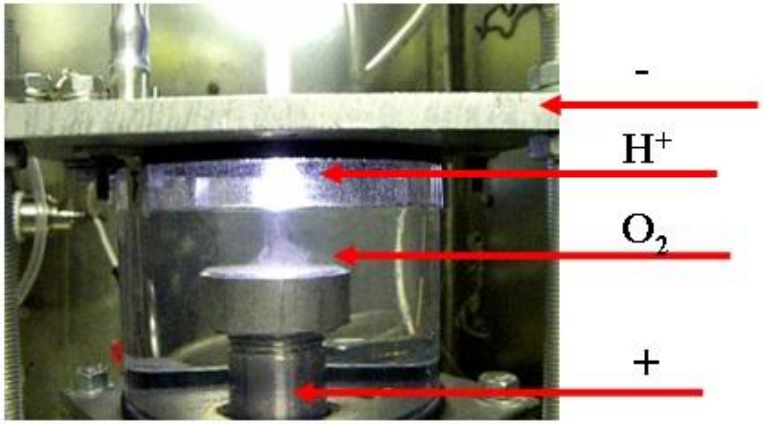
Breakdown

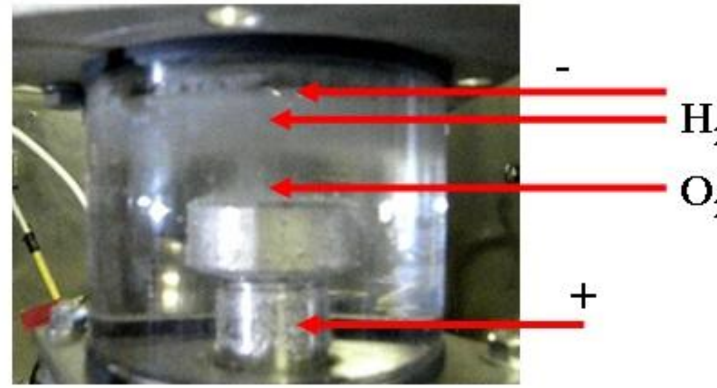
Discharge burning



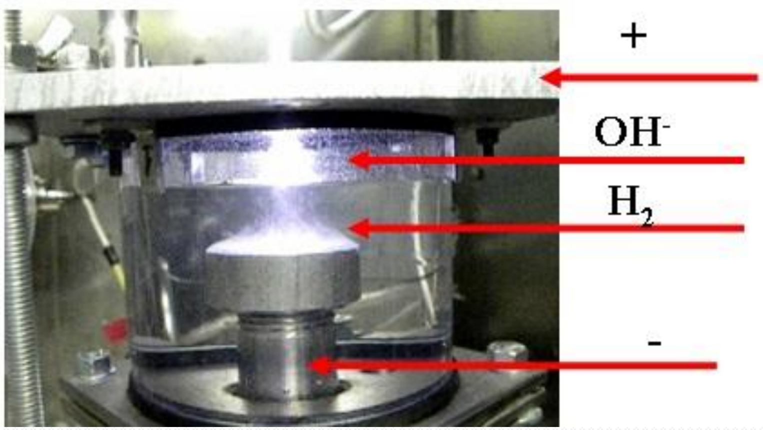
Electrochemical phenomena

"Solid" Cathode, liquid – H_2O, gas – Air, gas flow – 110 cm^3/s, I_d = 300 mA





"Liquid" Cathode, liquid – H_2O, gas – Air, gas flow – 110 cm^3/s, I_d = 300 mA



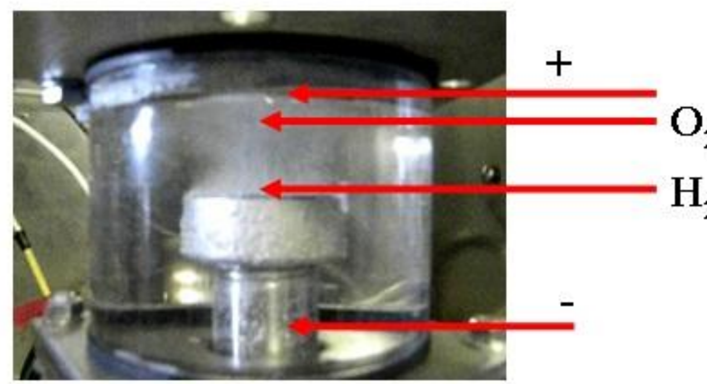


Figure 21: Photograph of hump model used for the study of turbulent boundary layer separation control using SDBD plasma actuators. (from He[34, 35])

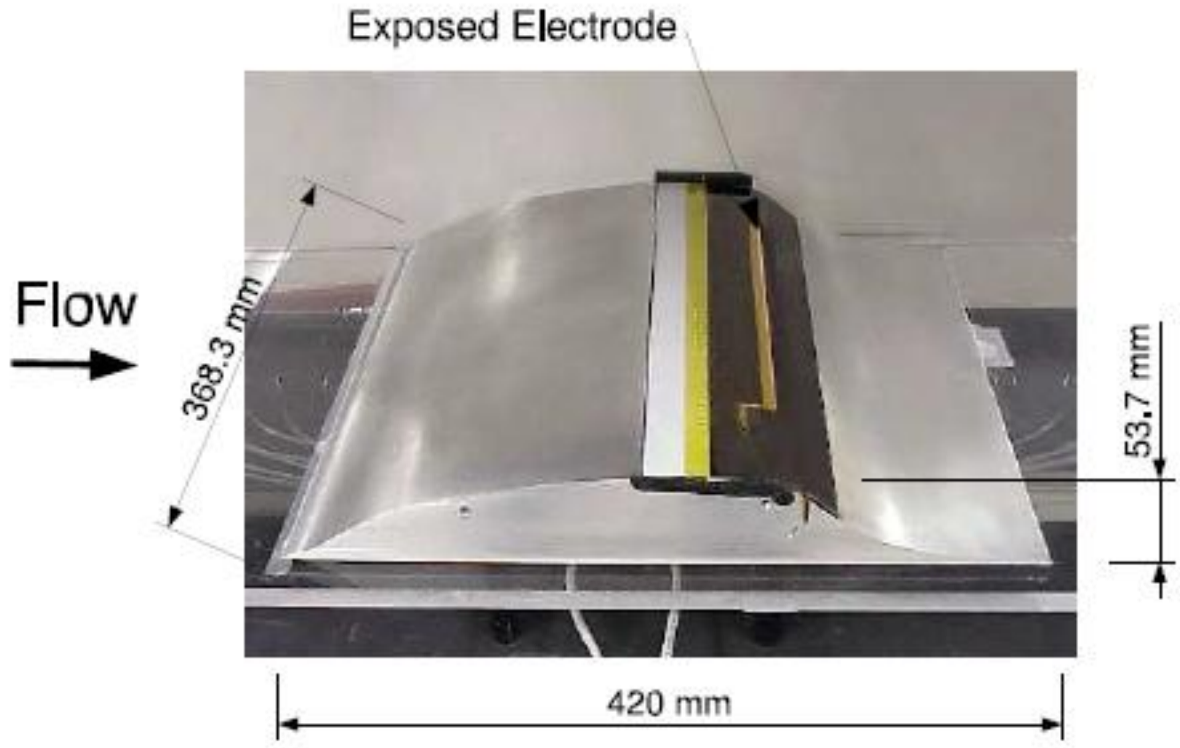


Figure 28: Visualization of the base flow over a periodic pitching NACA 0015 airfoil captured at different angles of attack in the cycle. (from Post [92])

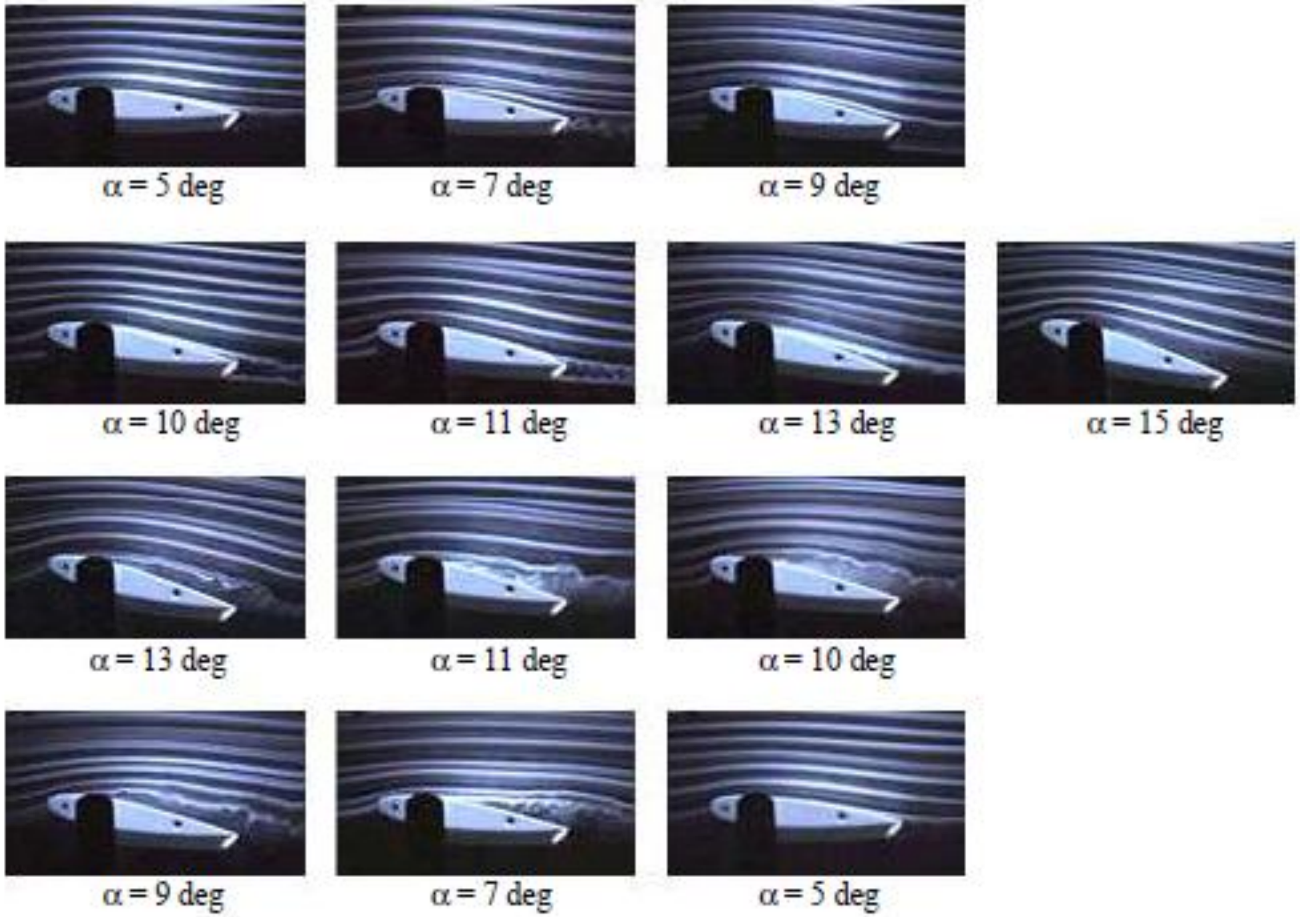
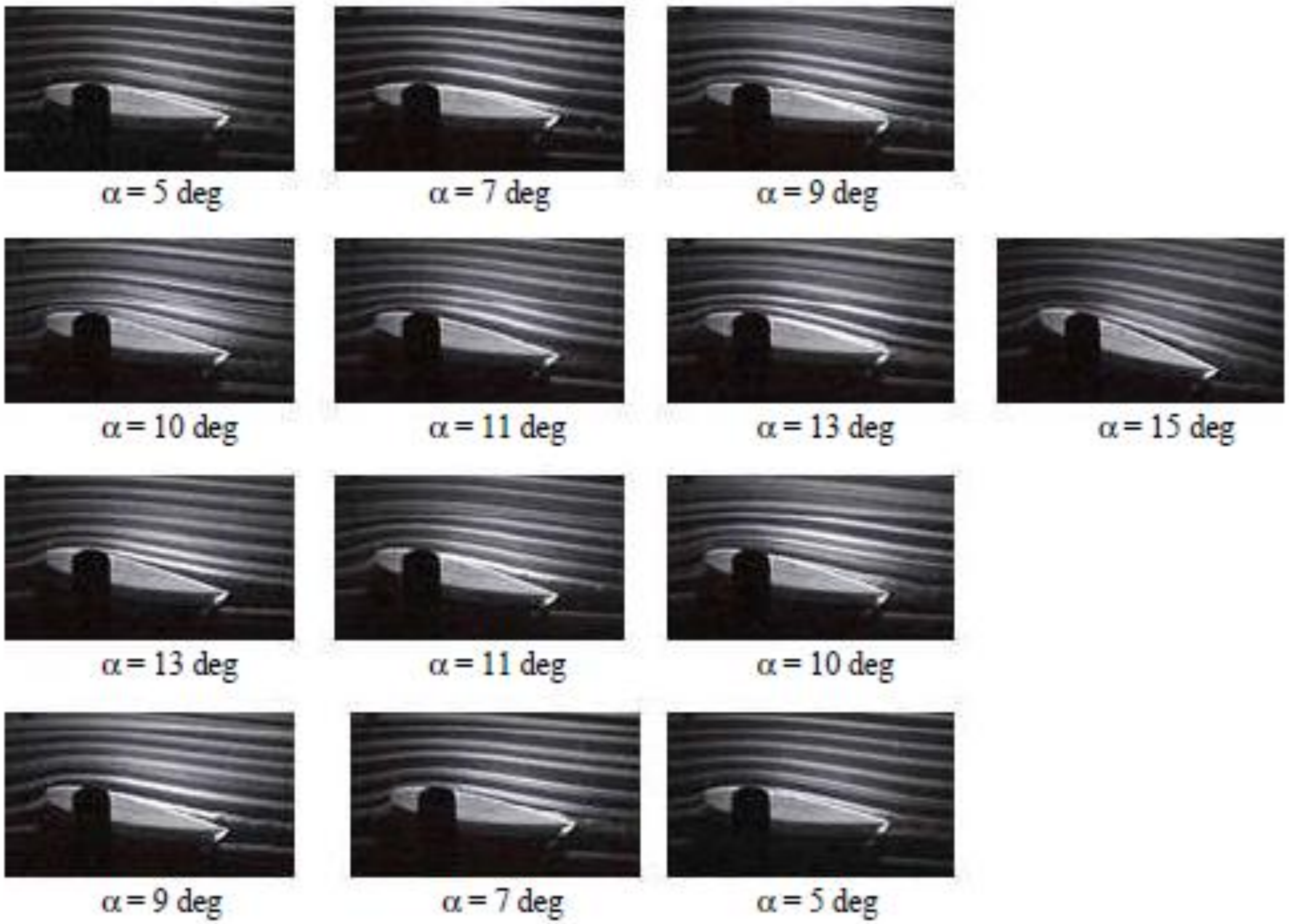


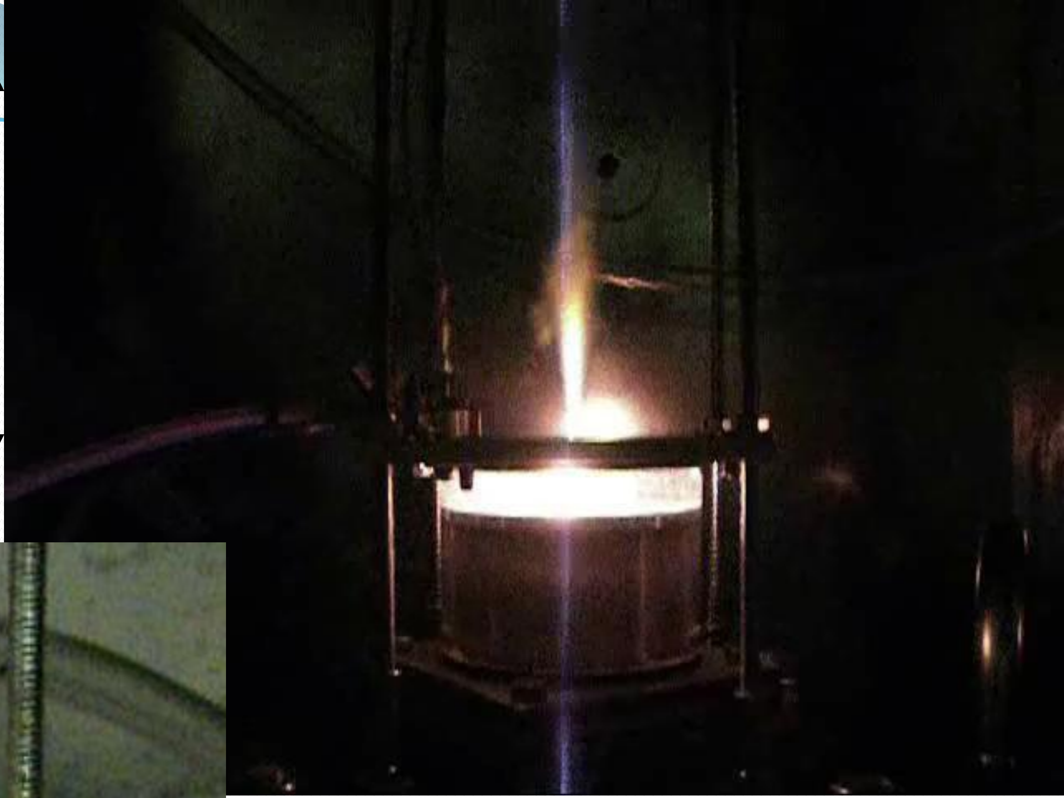
Figure 29: Visualization of the flow over a periodic pitching NACA 0015 airfoil captured at different angles of attack in the cycle with a leading-edge plasma actuator. From Post [92].

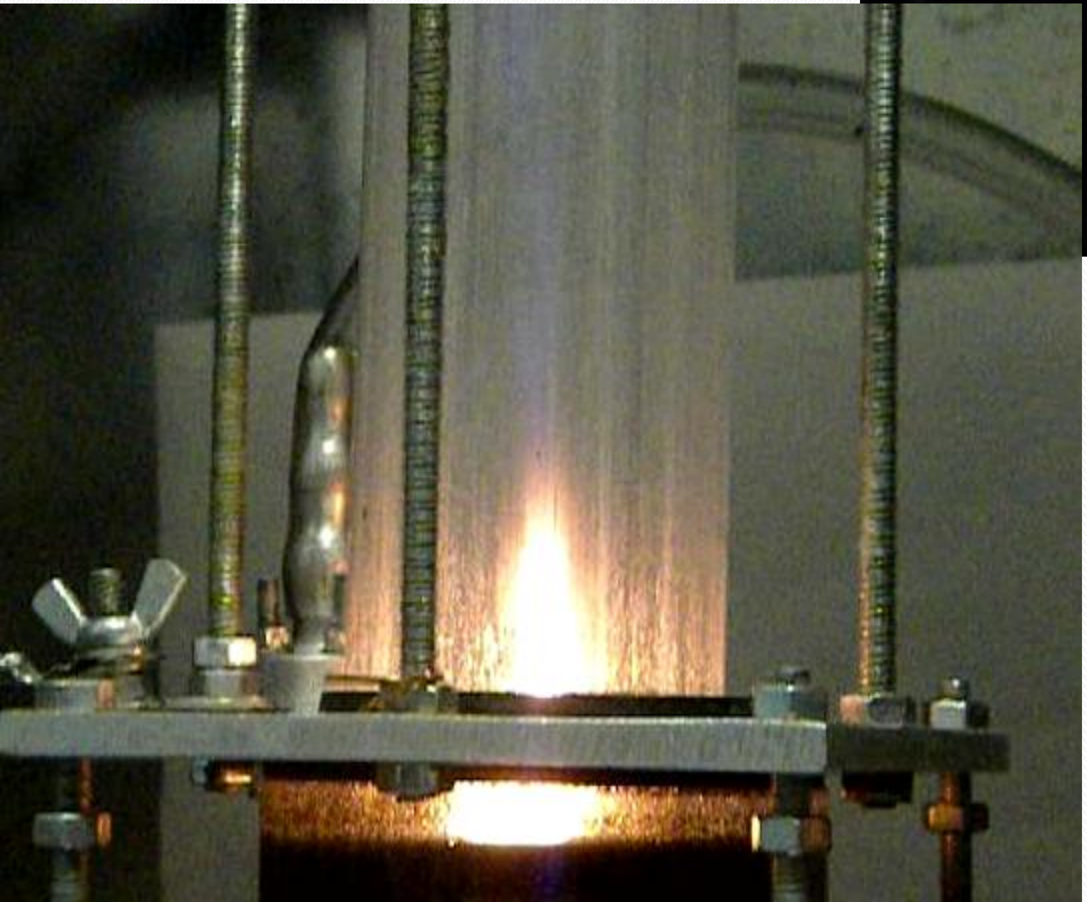


Experimental: Bioethanol and bioglicerol burning in TORNADO-LE

20 cm

$C_2H_5OH : H_2O = 1 : 9{,}5$



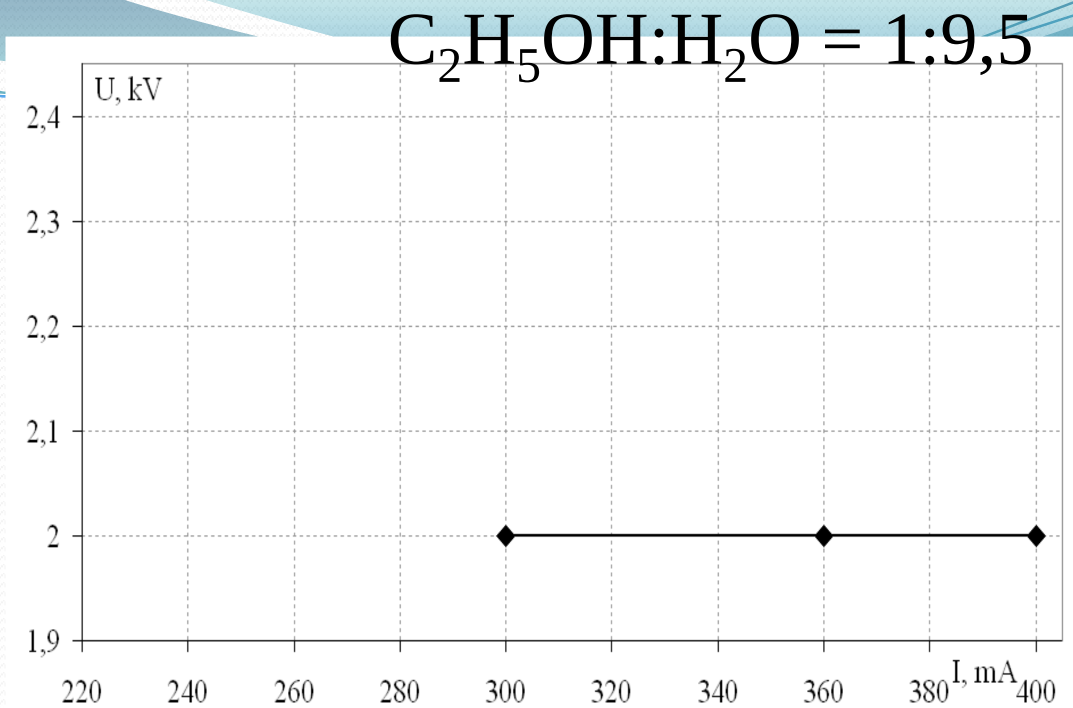


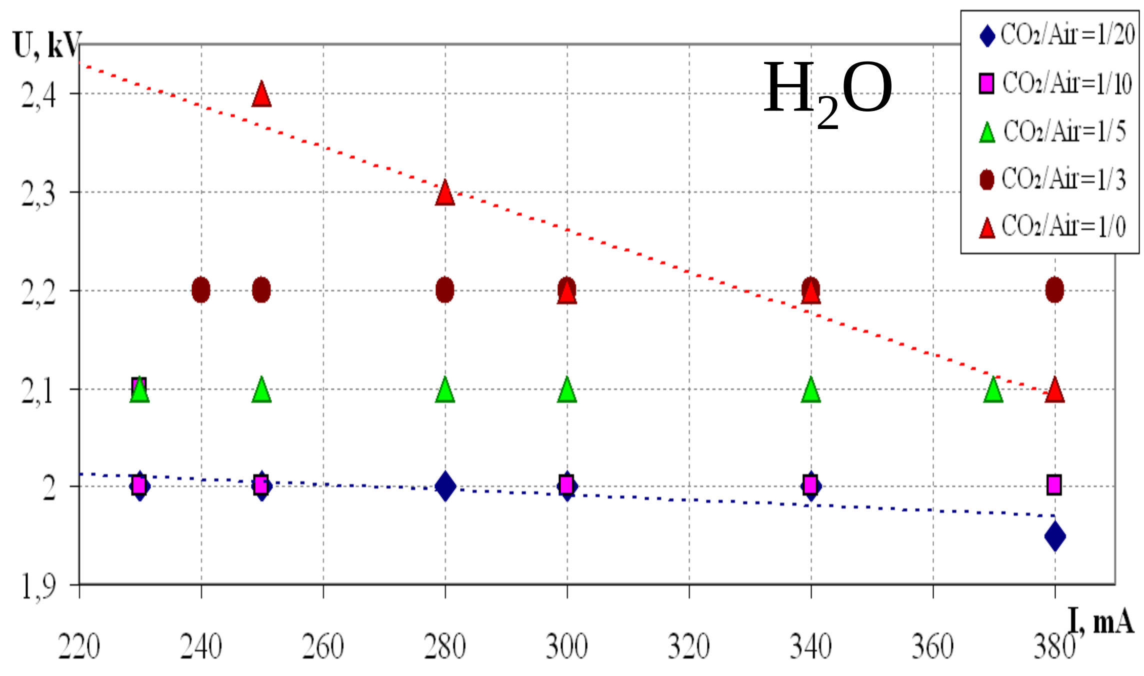
Bioglicerol +H_2O = 9+1

Basic results:

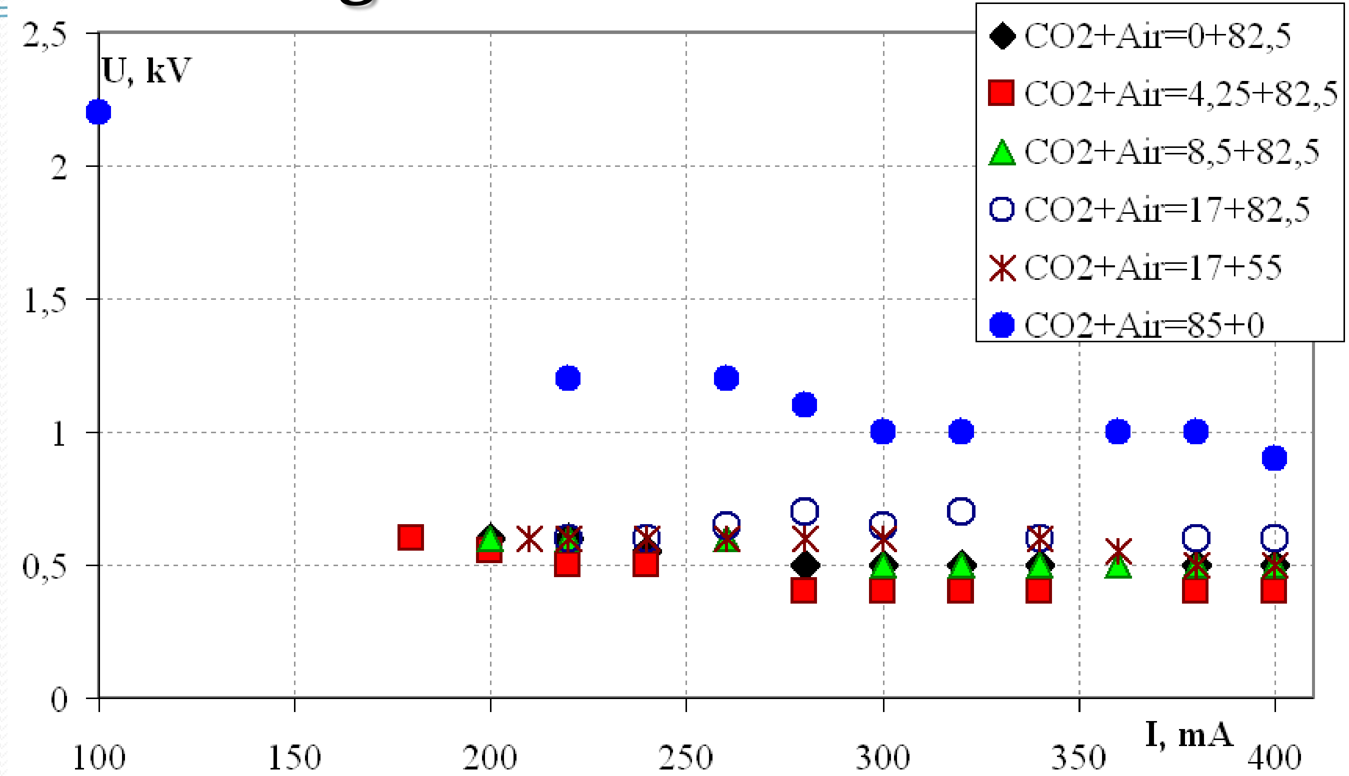
Current-voltage characteristics of TORNADO -LE

The "tornado" type reverse vortex gas flow is formed by gas flow, which is a mixture of air with CO_2 in varying proportions. Ratio of CO_2/Air is changed in the range from 1/20 to 1/3, and in the case of ethanol and 1/0 in the case of water. Current varied in the range from 230 to 400 mA. The initial level of the working liquid is the same in all cases.





Basic results: Current-voltage characteristics of TORNADO -LE



Bioglicerol ↓

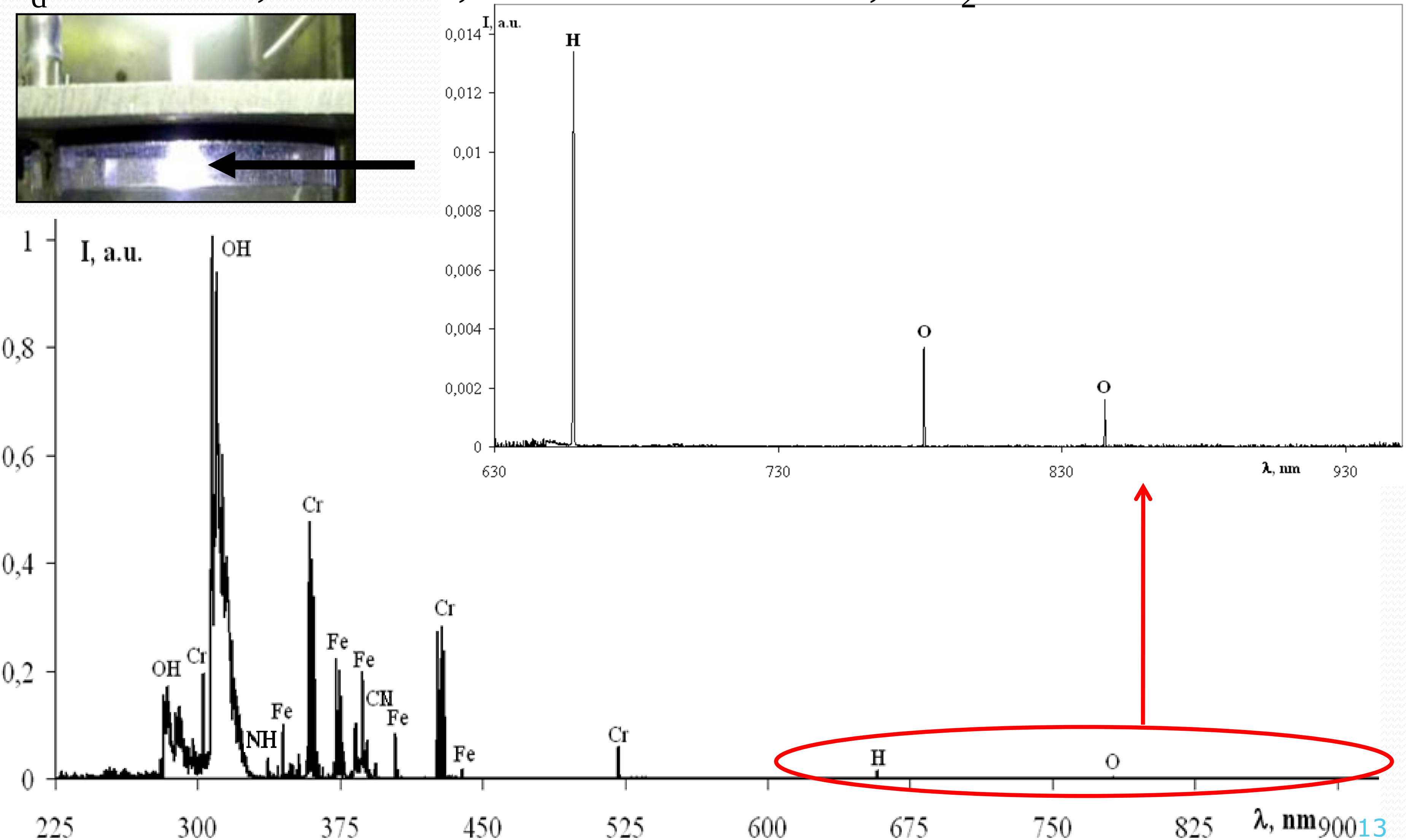
I=200÷400 mA	U, kV
CO_2+Air=0+82,5	0,3
CO_2+Air=4,25+82,5	0,6
CO_2+Air=8,5+82,5	0,6 - 0,8
CO_2+Air=17+82,5	0,7
CO_2+Air=17+55	0,6 - 0,7

↑

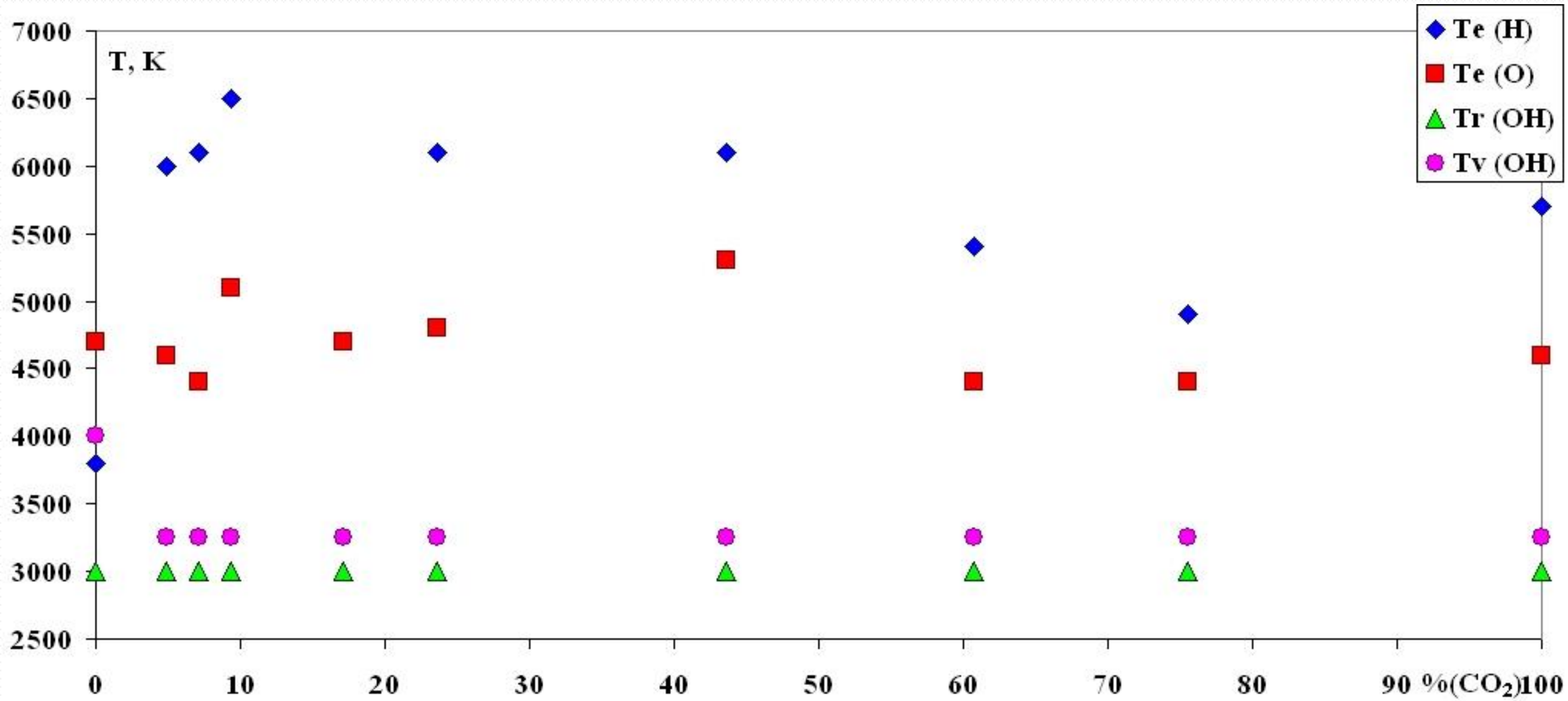
Bioglicerol+H_2O = 9+1

Basic results: The emission spectra of plasma

Spectrum of the plasma in TORNADO-LE plasma-liquid system, where the working liquid is $C_2H_5OH:H_2O=1:9,5$. Working gas – CO_2/Air 1/10, I_d = 300 mA, U = 2 kV, airflow - 82.5 cm^3/s, CO_2 - 4.25 cm^3/s.

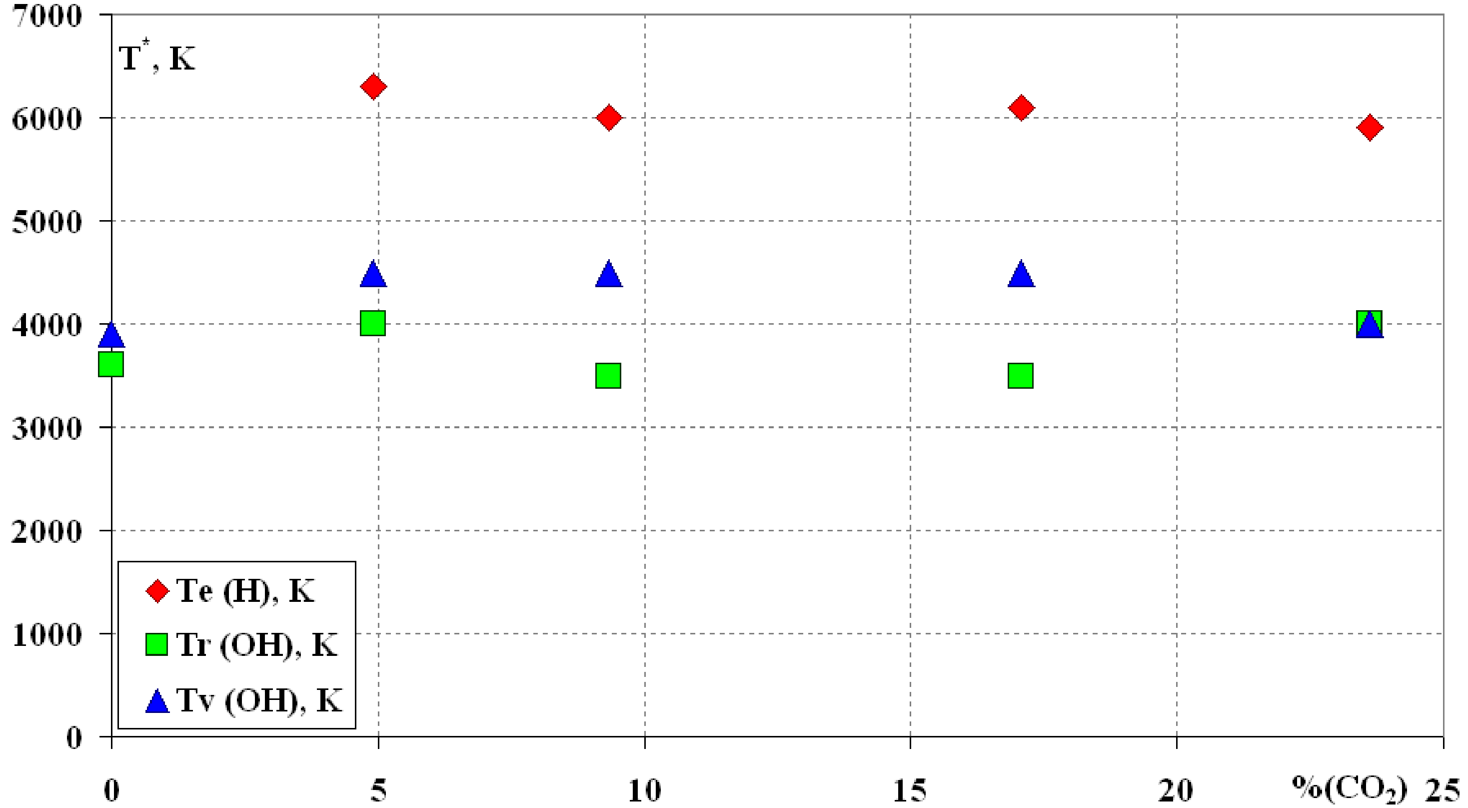


Basic results: Electronic T^*_e, vibrational T^*_v and rotational T^*_r temperatures of plasma components



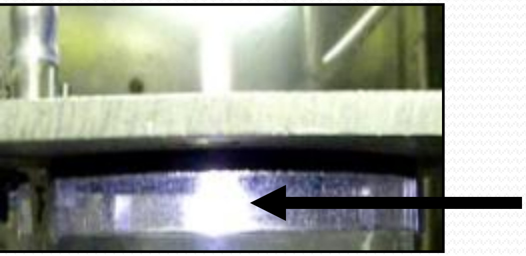
Population temperatures of excited electron, vibration and rotational levels of plasma components at different ratio of CO_2/Air in the working gas. Working liquids – H_2O.

Basic results: Electronic T^*_e, vibrational T^*_v and rotational T^*_r temperatures of plasma components

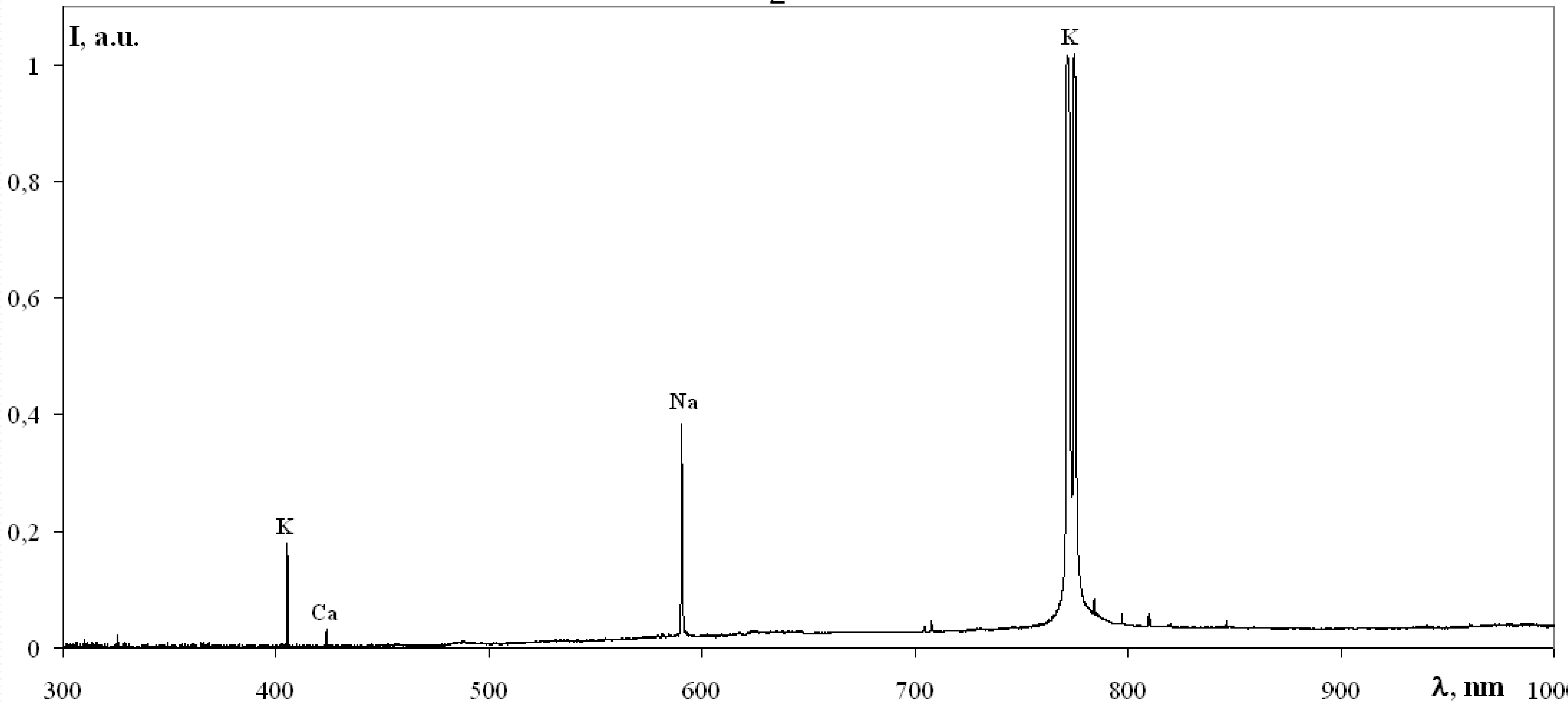


Population temperatures of excited electron, vibration and rotational levels of plasma components at different ratio of CO_2/Air in the working gas. Working liquids – bioethanol.

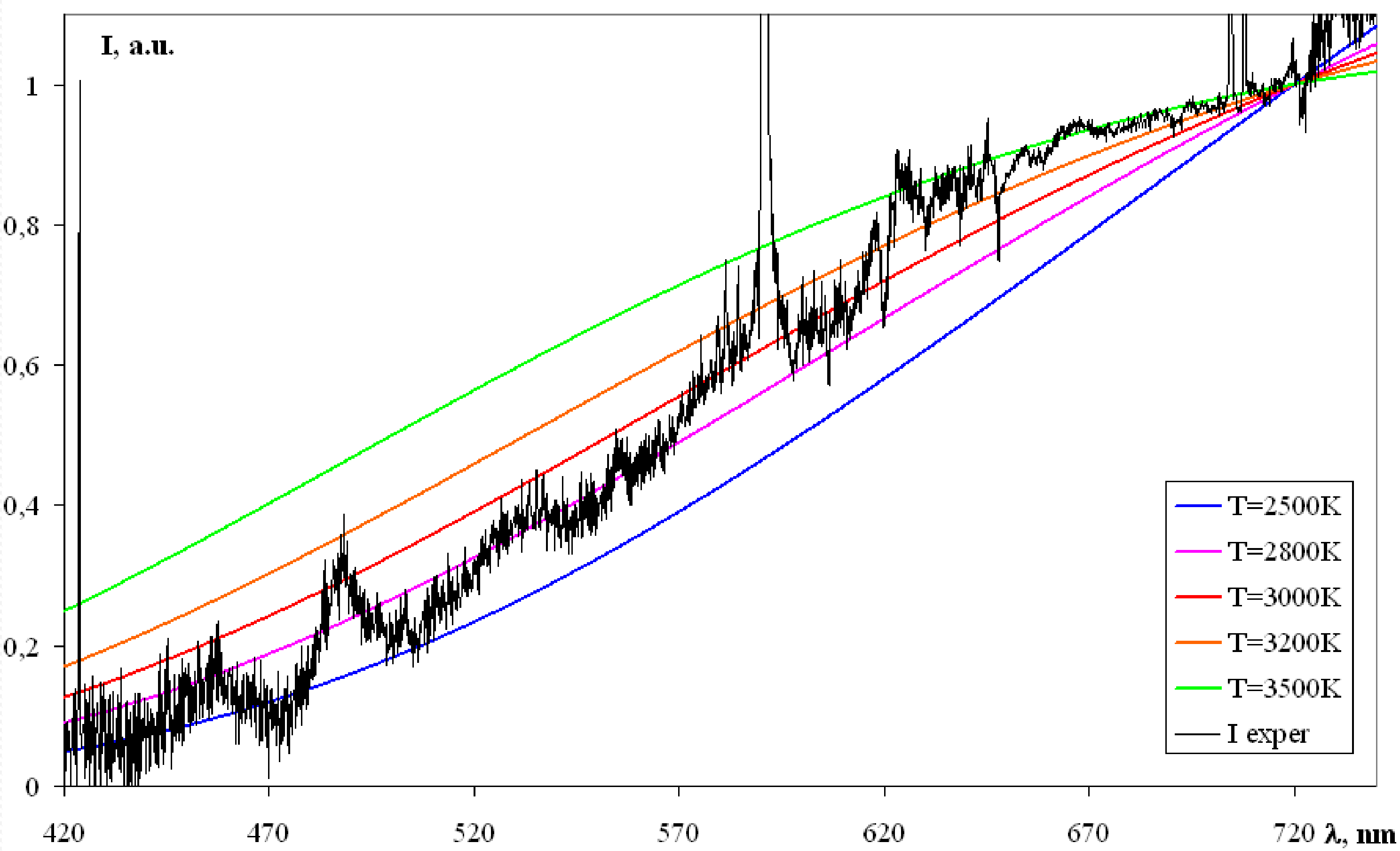
Basic results: The emission spectra of plasma



Spectrum of the plasma in TORNADO-LE plasma-liquid system, where the working liquid is $C_3H_5(OH)_3$. Working gas - a mixture of CO_2/Air = 1/5, I_d = 300 mA, U = 0,6 kV, air flow - 82.5 cm^3/s, the flow of CO_2 - 8.5 cm^3/s.

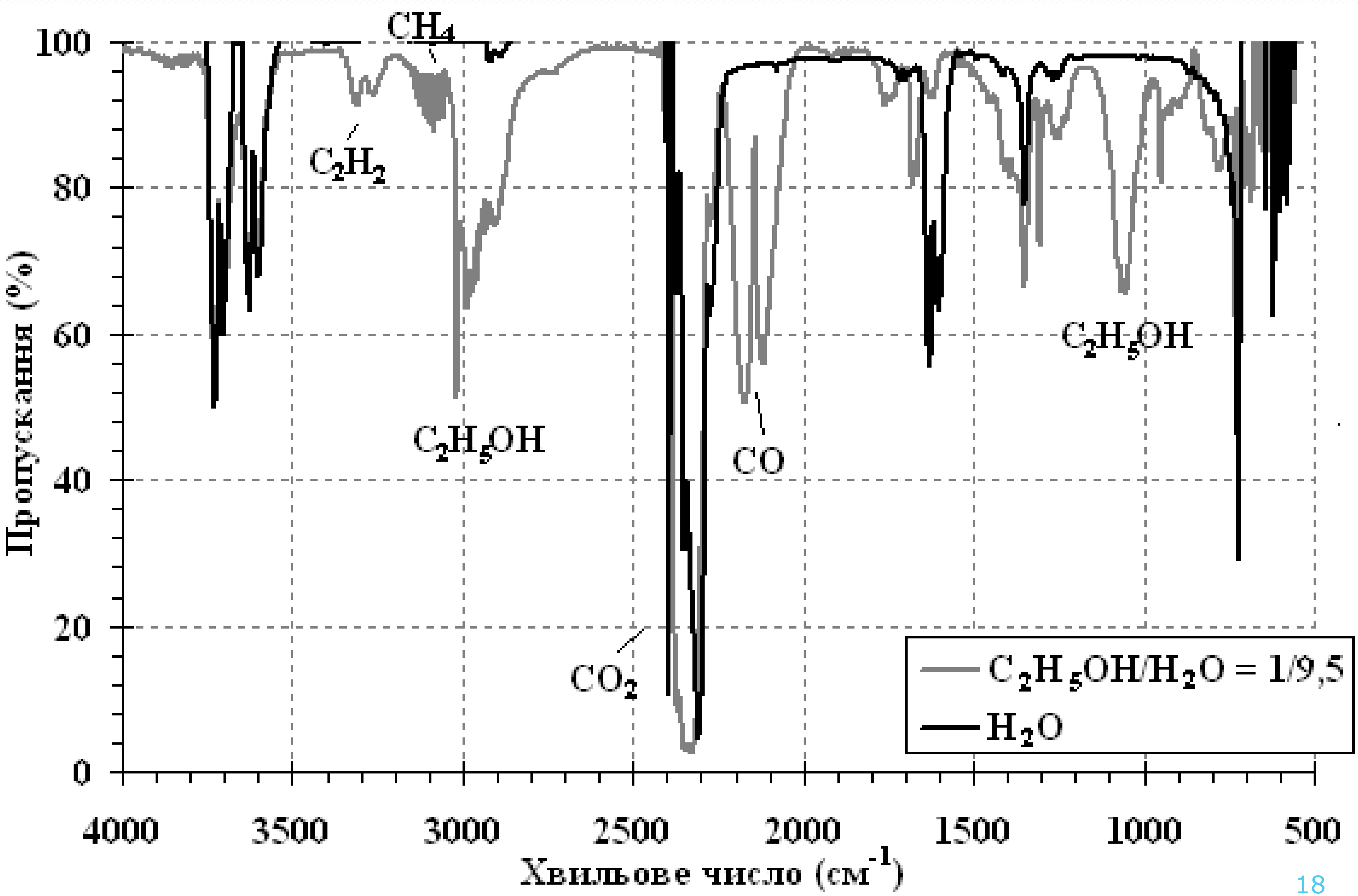


Basic results: Temperatures of plasma component

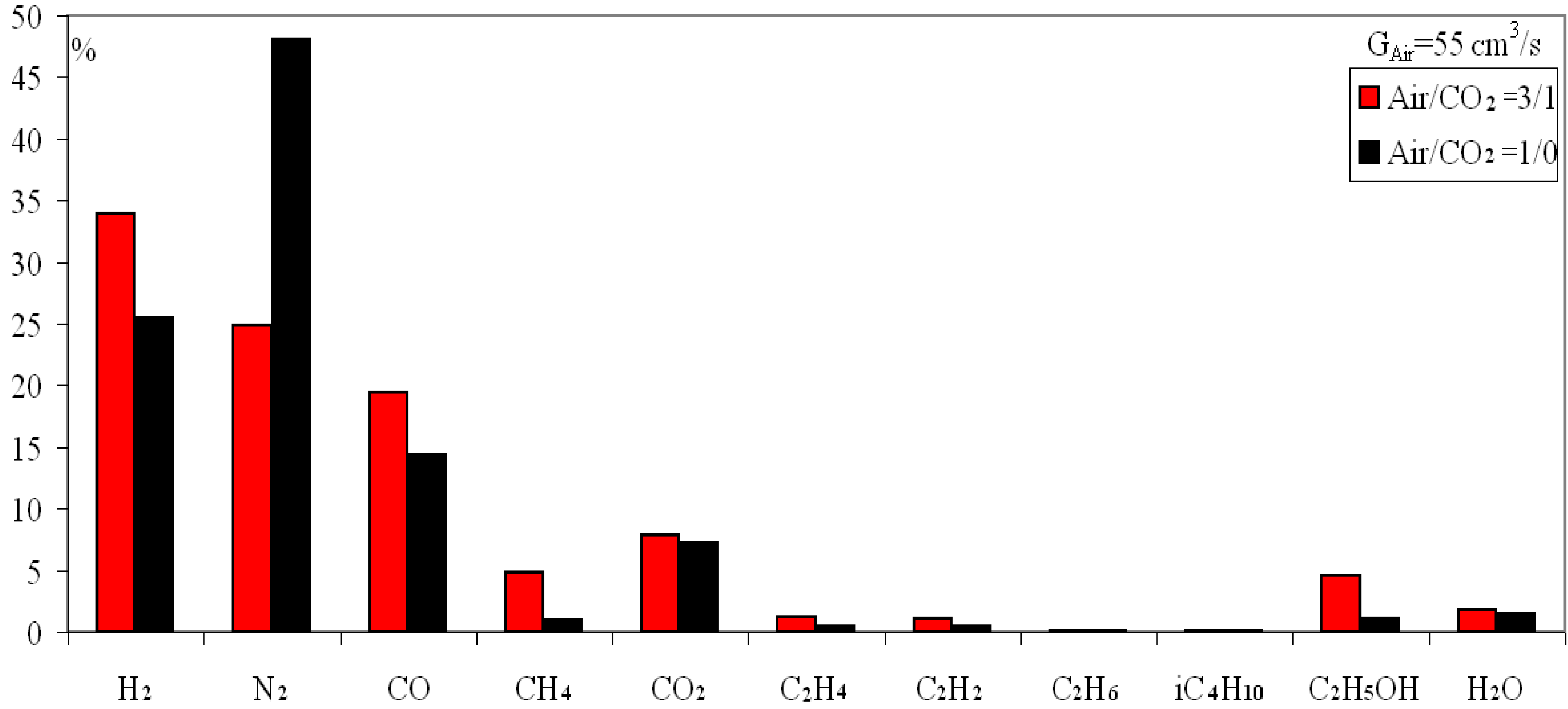


The comparison of experimental results with by the calculated radiation spectrums of blackbody.

Basic results: ***Infrared spectrophotometry (IRS) of output gas*** I=300 mA, U=2,2 kV, G_{Air}= 55 cm^3/s, G_{CO2} = 17 cm^3/s

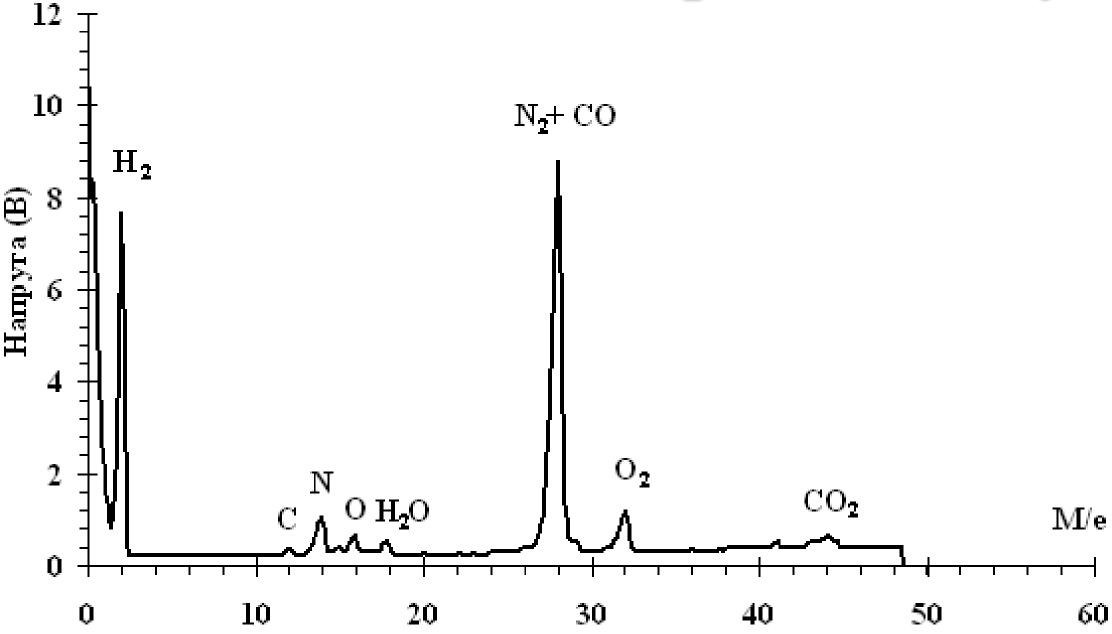


Basic results: Gas chromatography of output gas



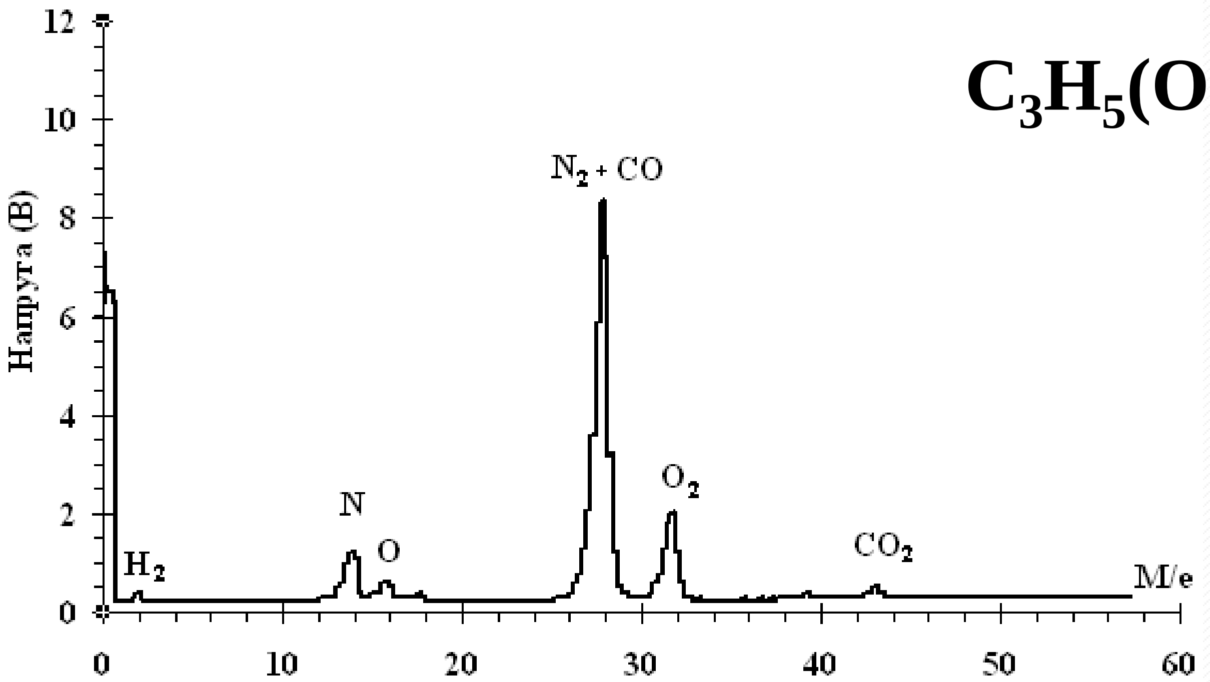
Comparison of the output gas products in the conversion of bioethanol with and without the addition of CO_2. I = 300 mA, G_{Air}= 55 cm^3/s. Liquid – $C_2H_5OH : H_2O$ = 1 :

Basic results: Mass-spectrometry of output gas



$C_2H_5OH : H_2O = 1 : 9,5$
(1 : 3, Vol)

I=300 mA,
U=2,2 kV
G_{Air}= 55 cm^3/s,
G_{CO2} = 17 cm^3/s

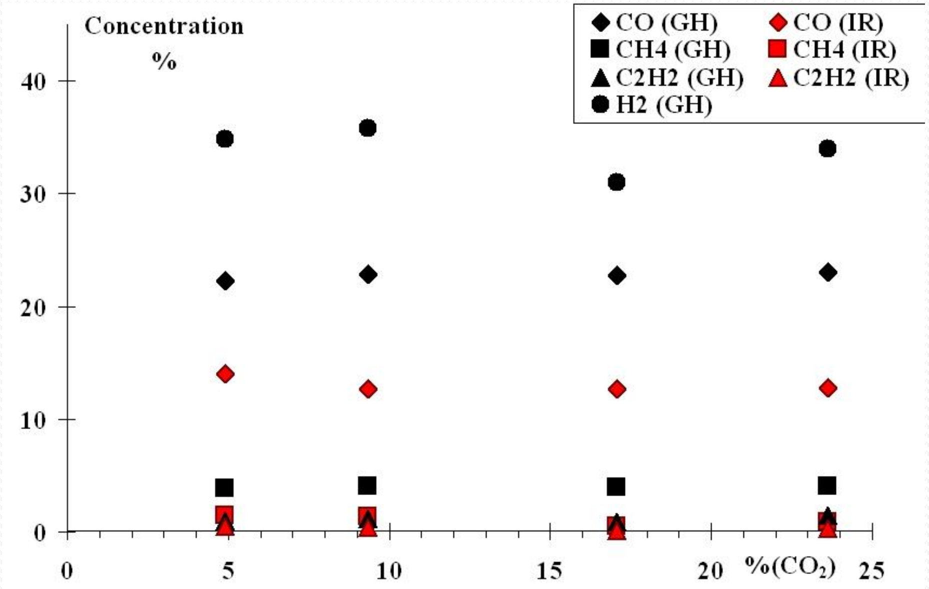


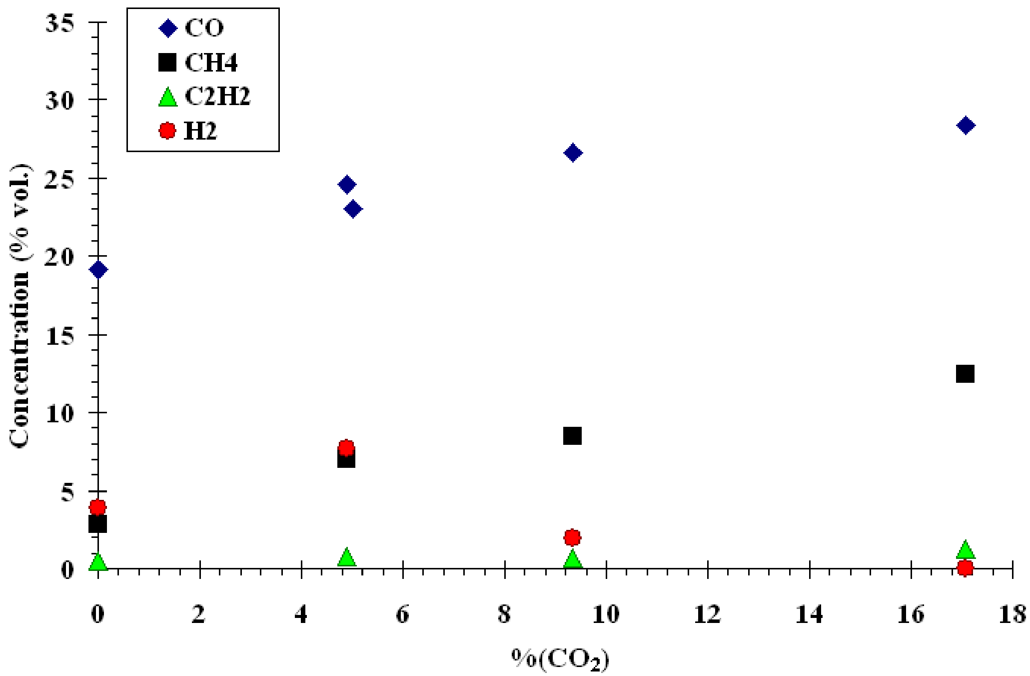
$C_3H_5(OH)_3+H_2O = 9+1$, Vol

I=300 mA,
U=0,6÷0,8 kV
G_{Air}= 82,5 cm^3/s,
G_{CO2} = 8,5 cm^3/s

Basic results: Concentration of output gas

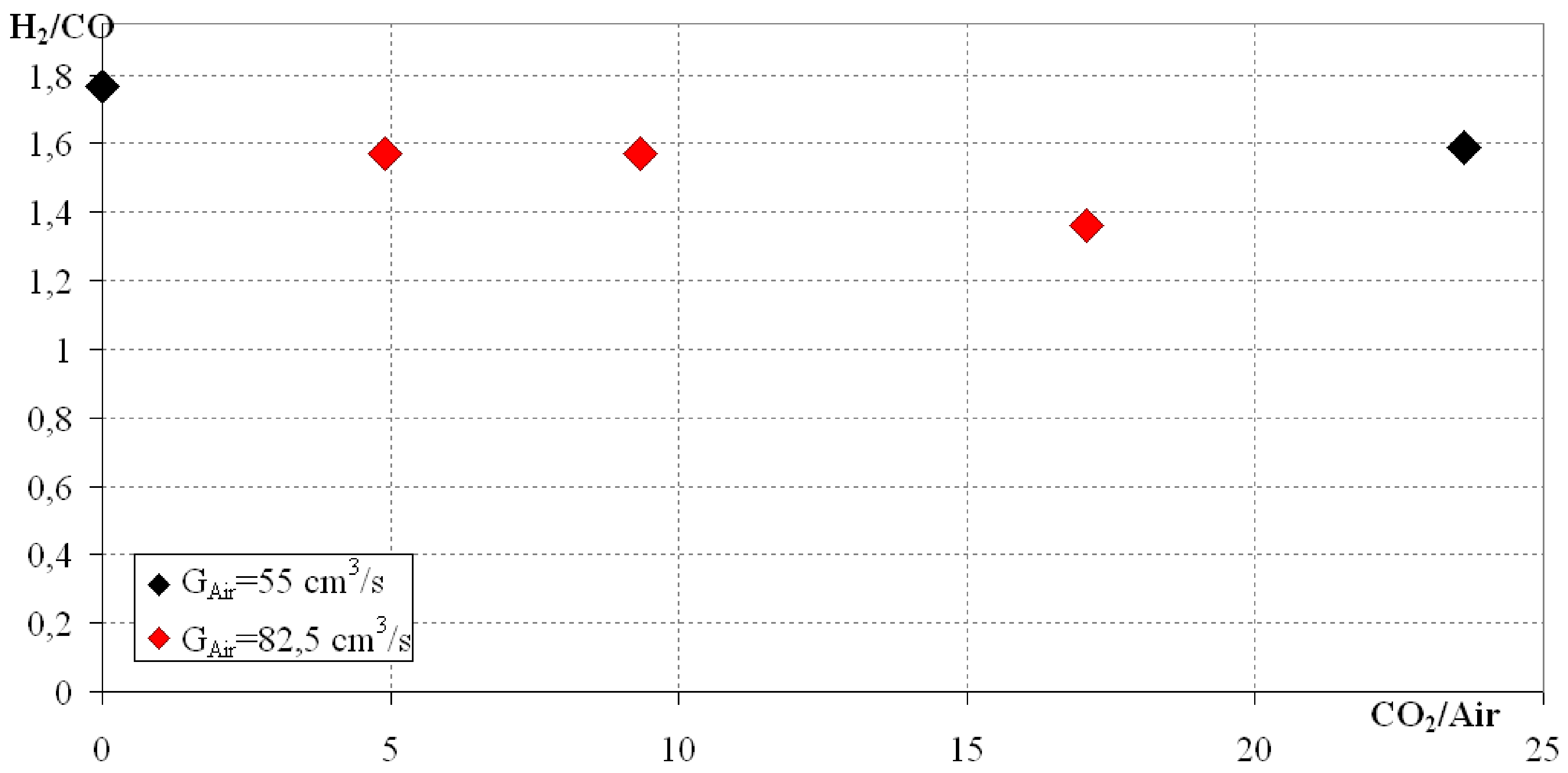
Concentration of main components of the output gas for **bioethanol** →





Concentration of main components of the output gas for **bioglycerol** ←

Basic results: Syngas ratio ($[H_2]/[CO]$)

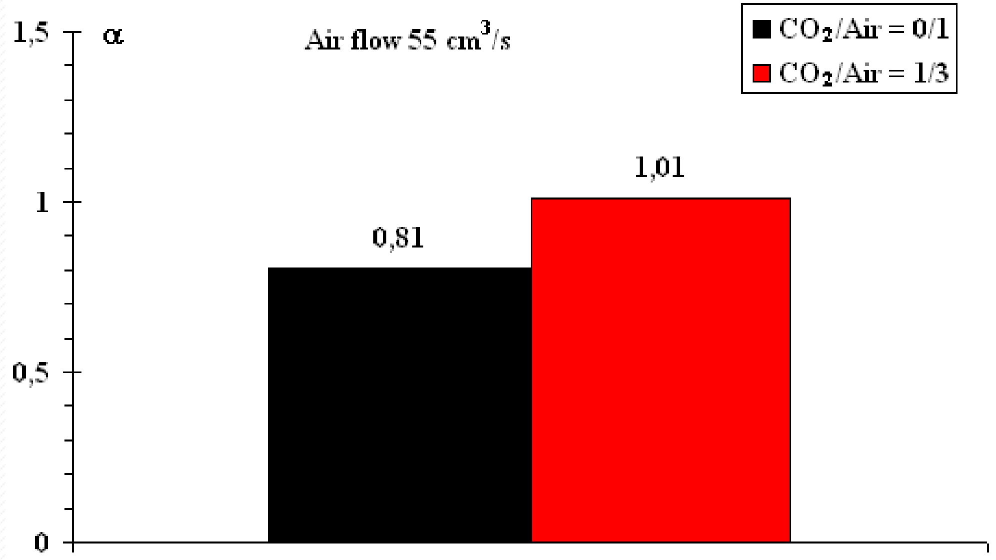


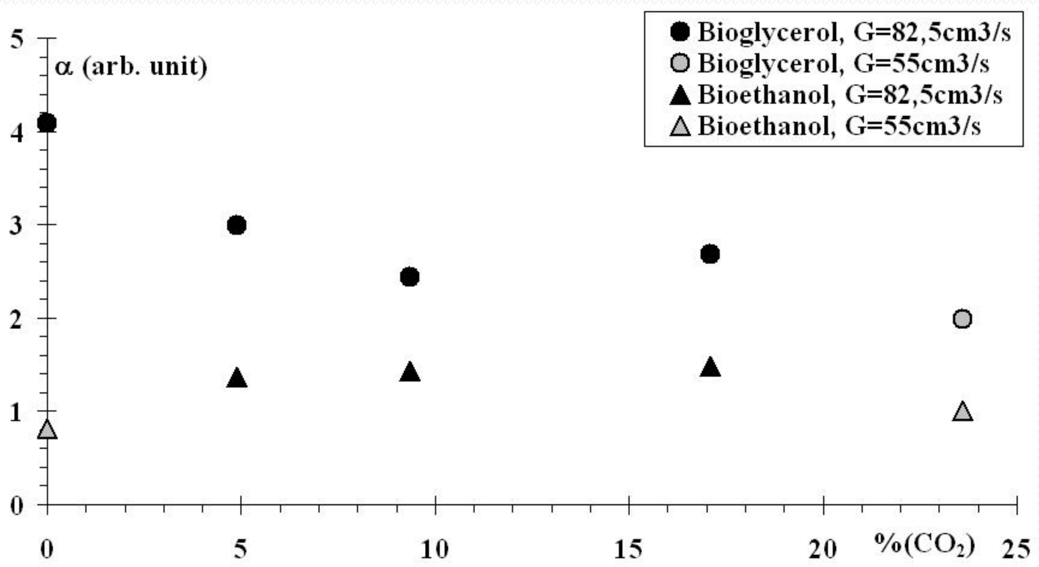
Found that adding CO_2 weakly affects $[H_2]/[CO]$ ratio

Basic results: Coefficient of electrical energy transformation

$C_2H_5OH : H_2O = 1 : 9,5$

$$\alpha = \frac{Q_{syngas}}{Q_{plasma}}$$





Bioglicerol+H_2O = 9+1

General conclusions

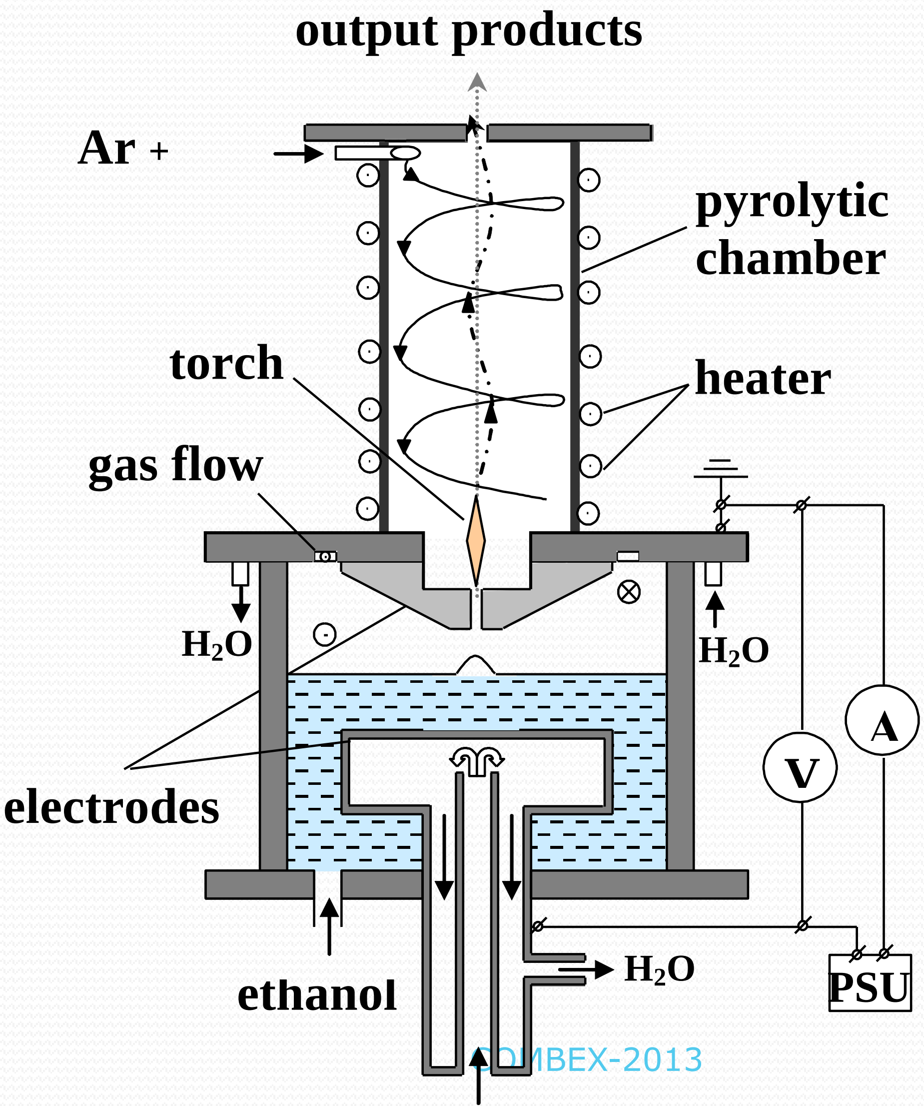
On the base of our results in bioethanol and bioglycerol CO2-reforming by "TORNADO-LE" PLS, we can say that:

1. The possibility of reforming of hydrocarbons with significant viscosity (such as bioglycerol) is existing in this system;

2. This process has special features, connected with CO_2 retarding role in the conversion components combustion;

3. All the diagnostic methods, used in the "TORNADO-LE" PLS, indicate that there're no NO_x compounds in the bioethanol and bioglycerol reforming products.

Plasma-liquid system of "Tornado" type combined with the reaction pyrolytic chamber

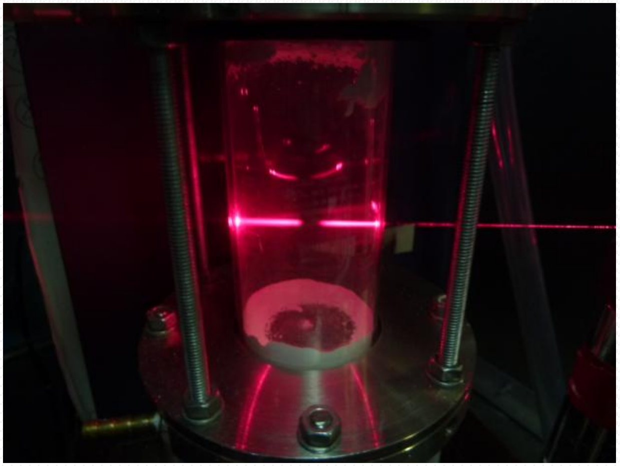


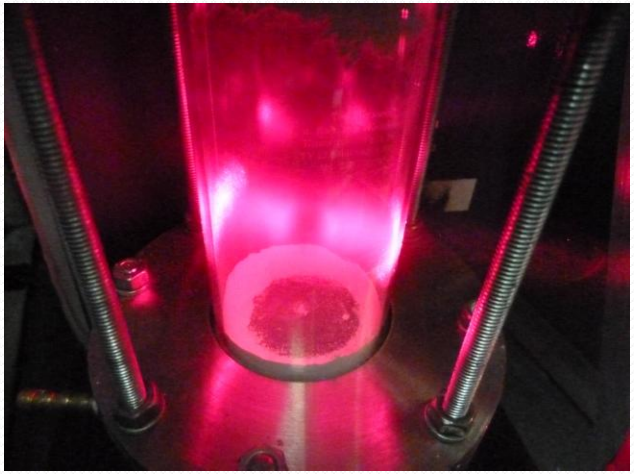
Solid arrows representing three-dimentional sketch of input rotating downflow near the walls.

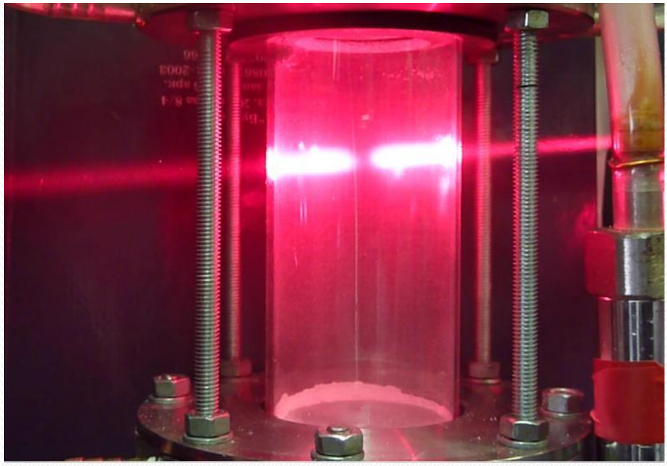
Dashed line representing the output rotating upflow on the axis (helical).

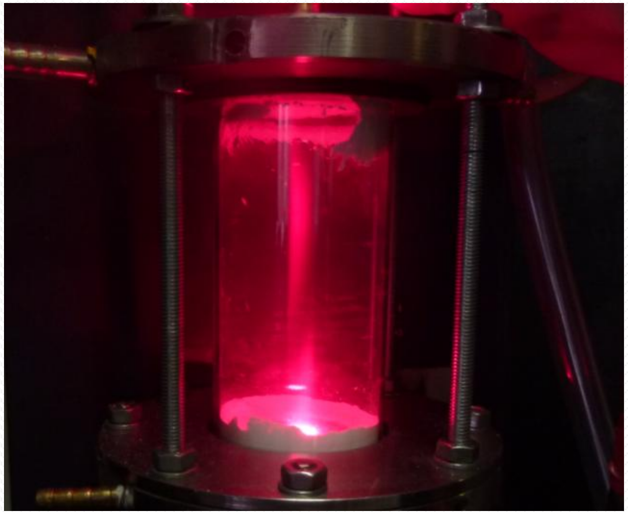
Dotted line representing the axial gas flow.

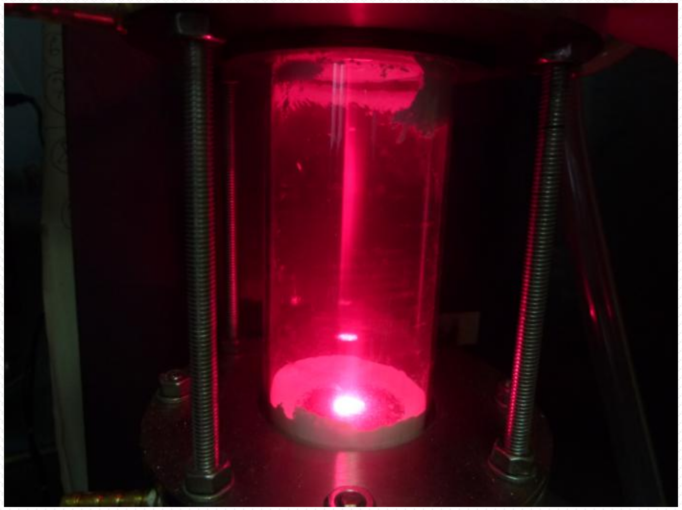
Structure of gas flow in the reaction chamber <u>without axial gas flow</u>, for example argon with micro dust

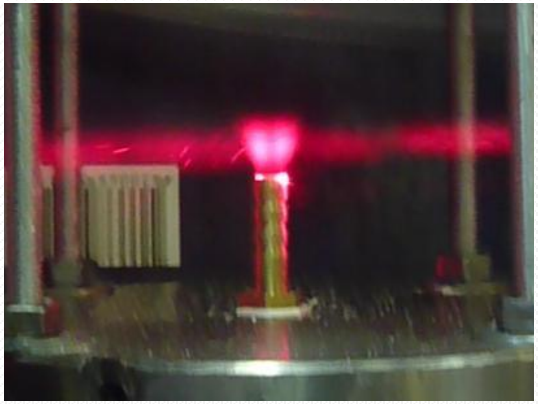










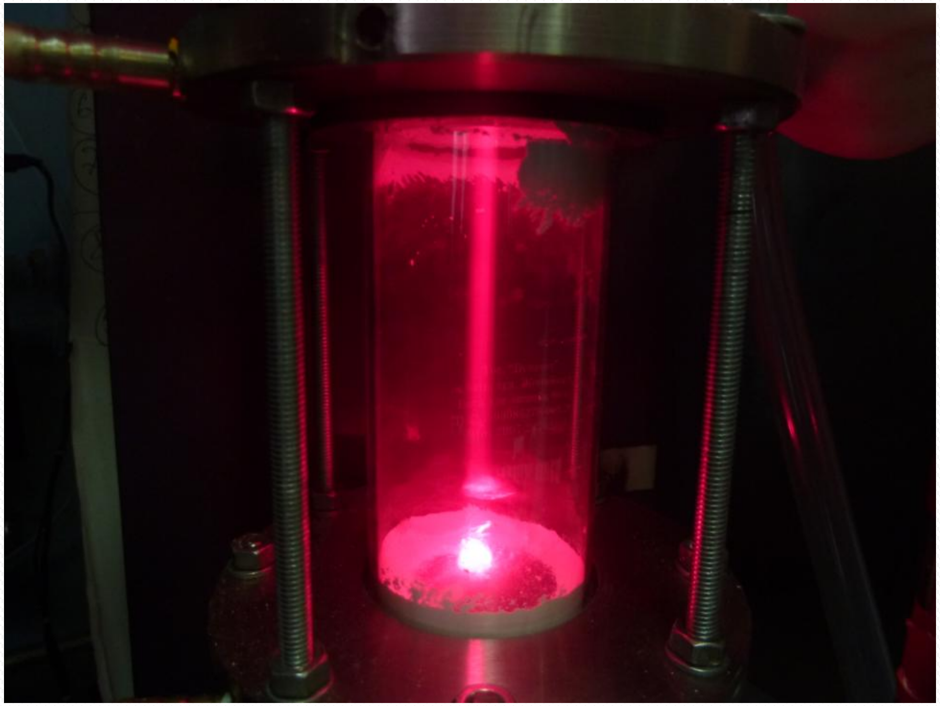


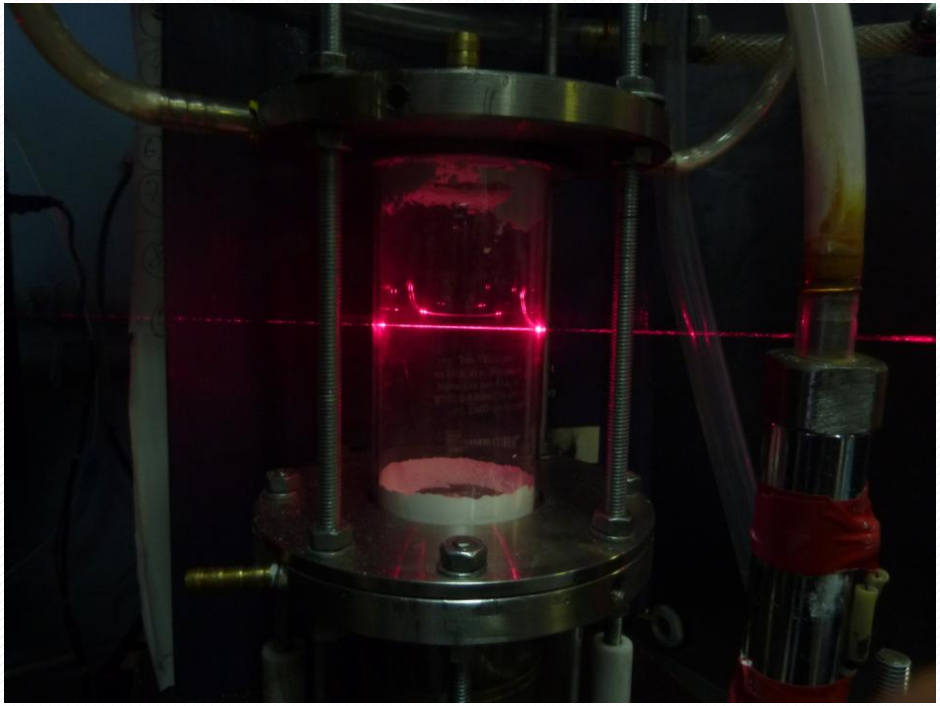
In upflow at the center of the camera, there is a helical void – a dust-free region with a diameter of about 5mm.

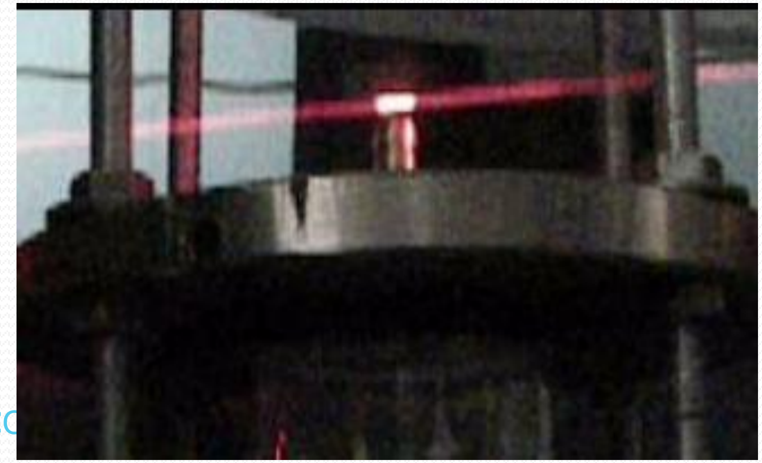
The outlet flow also have a void structure

(For outlet ∅ 4 mm, by increasing the outlet to 8 mm void in the output stream disappears).

With axial gas flow, from plasma-liquid chamber, void at gas flow in the reaction chamber **disappeare**







Thank you for attention!

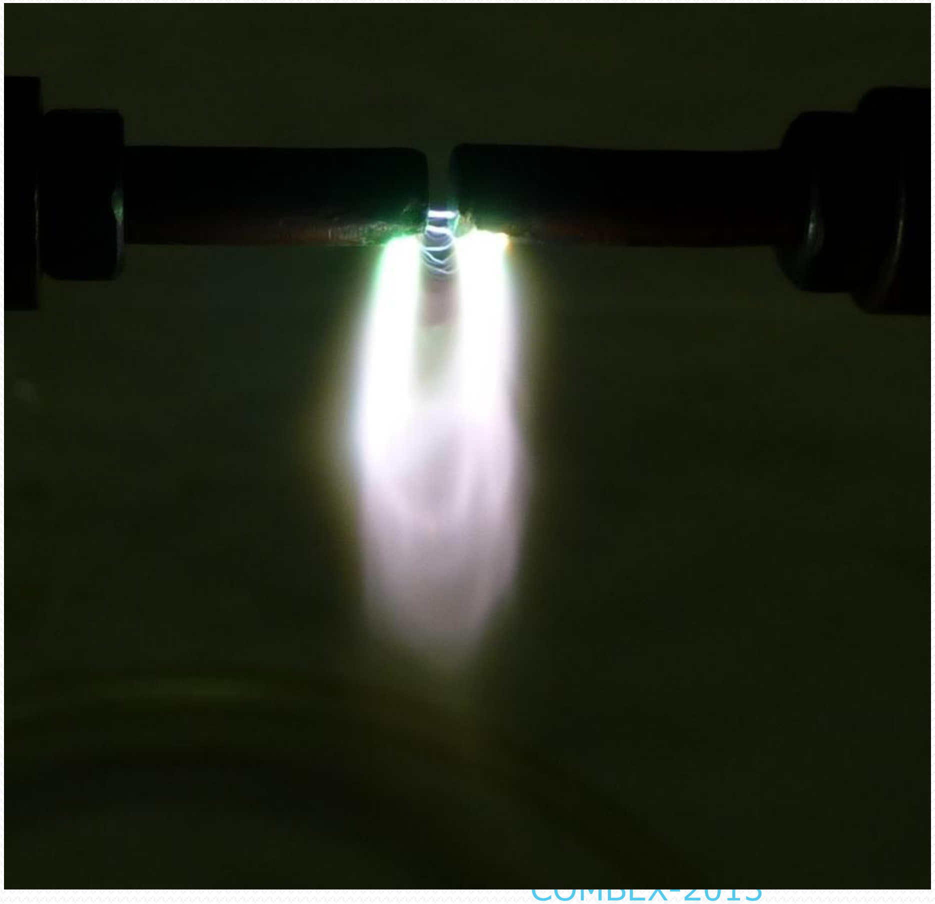
- The dynamic plasma-liquid systems with the DC discharge TORNADO-LE is quite efficient in plasma-chemical reforming of bioethanol and bioglicerol into hydrogen-rich synthesis gas. The main components of syngas are molecular hydrogen H_2 and carbon monoxide CO;
- Carbon dioxide adding leads to a significant increase the percentage of H_2 + CO (syn-gas) and CH_4 components in output gas. This may indicate that the CO_2 addition under the ethanol reforming increases the conversion efficiency, because CO_2 plays a role of the retarder in the system by reducing the intensity of the conversion components combustion;
- All the diagnostic methods, used in the PLS "TORNADO-LE" indicate that there're no NO_x compounds in the bioethanol and bioglycerol reforming products;

Conclusions:

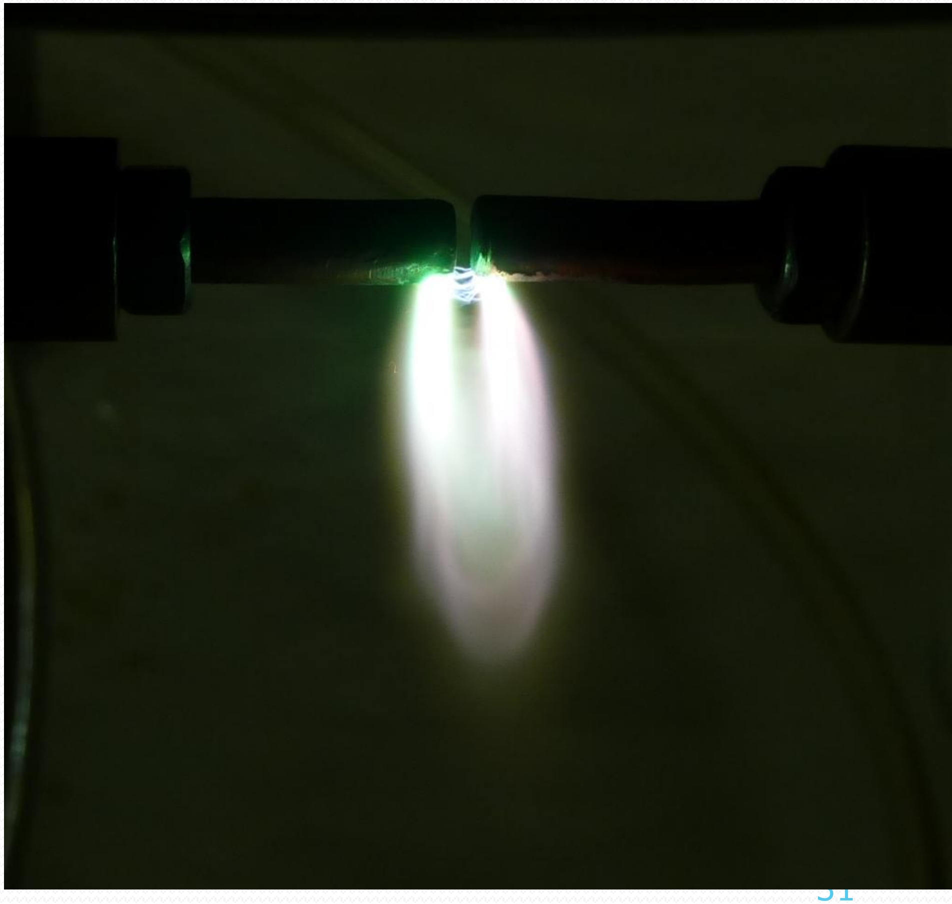
- The possibility of bioglycerol reforming in the PLS "TORNADO-LE" is shown. This gives a possibility to avoid environmental problems due to the bioglycerol accumulation during biodiesel production. It was found that dilution bioglycerol of water leads to the fact that formation of coking coal in the system decreases;
- The α coefficient in bioglycerol reforming is higher than ethanol reforming at the same ratios of CO_2/Air in the input gas. This may be connected with the lower power consumption on the plasma generation in case of bioglycerol reforming. Bioglycerol contains alkaline dash, which increases the bioglycerol conductivity. Bioglycerol reforming products contain mainly CO and hydrocarbons CH_4, C_2H_2, which also gives some contribution to energy yield.
- IRS spectra indicate that output gas obtained by ethanol solution conversion, contains such components as CO, CO_2, CH_4, C_2H_2. It was found that CO_2 adding reduces the CH_4 and C_2H_2 amount, but does not affect the amount of producted CO;

Photo of the transversal arc in air flow and in flow of air / ethanol mixture

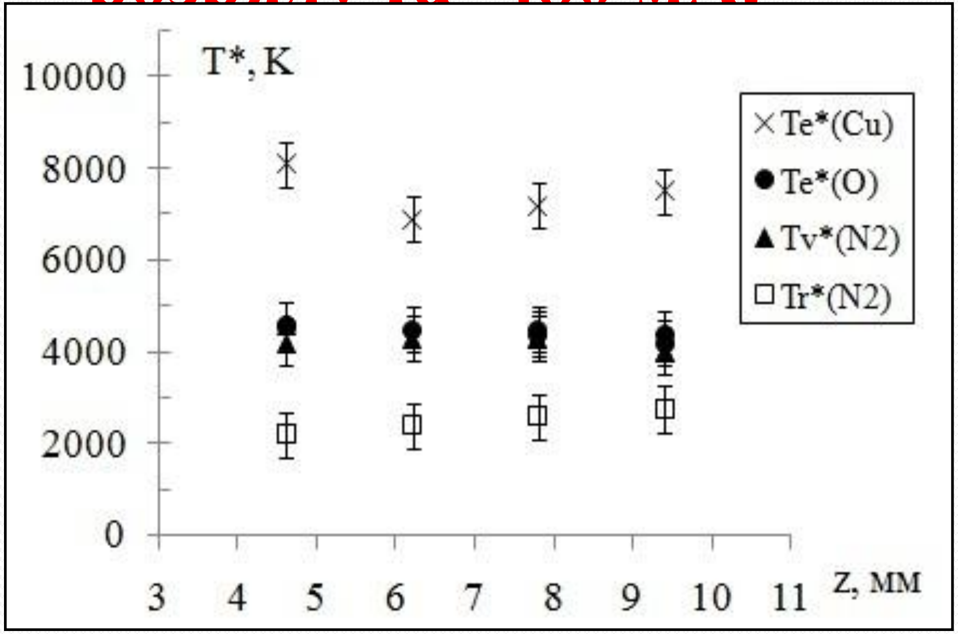
Air / ethanol mixture. I = 400 mA, U = 0,6 kV, G = 75 cm^3/s

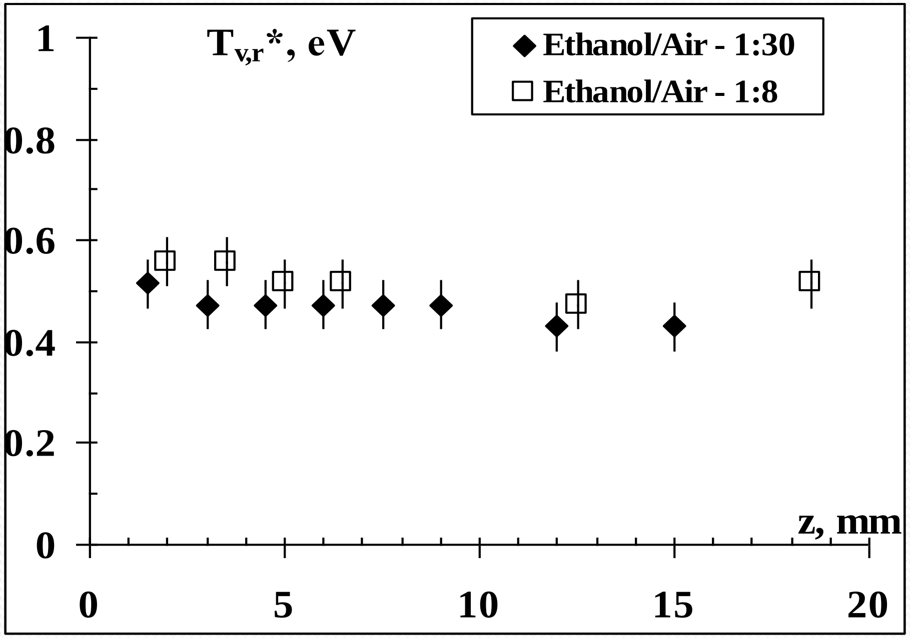


Air. I = 400 mA, U = 0,6 kV, G = 75 cm^3/s

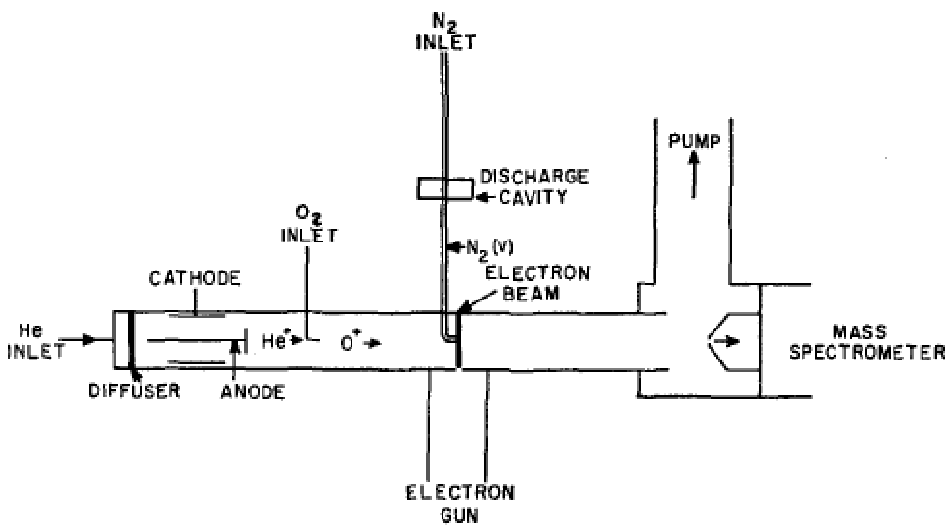


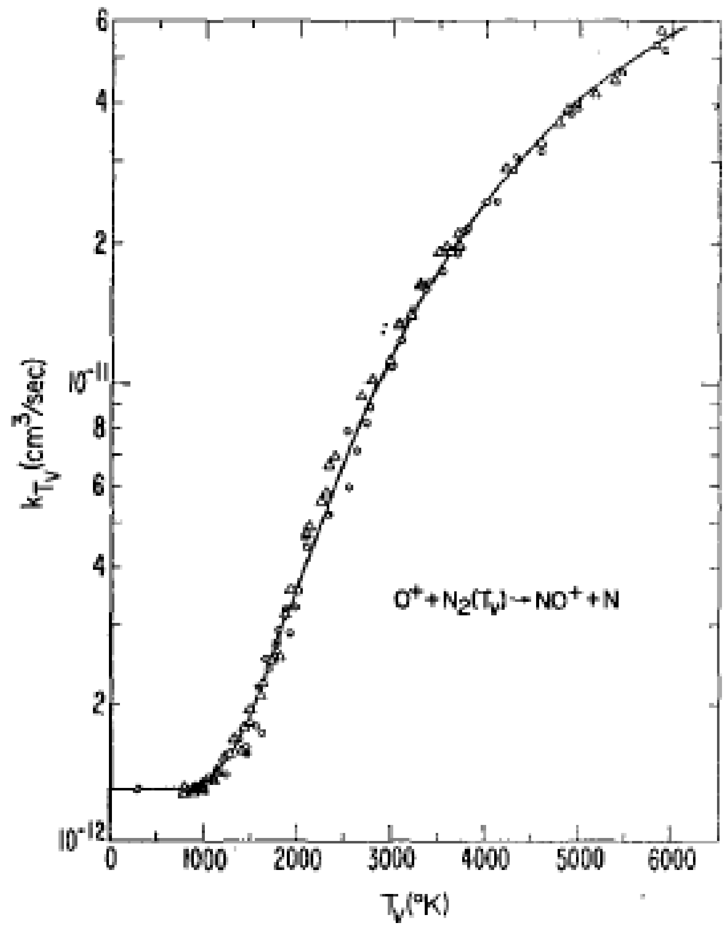
Температури заселення електронних збуджених рівнів атомів, коливальних та обертальних рівнів молекули азоту в плазмі ПД вздовж газового потоку G=75 см3/с: повітря, струм розряду Id=480 мА.





Reaction rate constant k_T • as a function of N vibrational temperature for the reaction $O^+ + N^*{}_2(v) \rightarrow NO^+ + N$ *[SCHMELTEKOPF A. L., FERGUSON E. E., FEHSENFELD F. C. Aterglow Studies of the Reactions He+, He(23S), and 0+ with Vibrationally Excited N2 // J. CHEM. PHYS.- (*





$$\frac{k_{T_v}(T_v = 6000\,K, T_{kin} = 300\,K)}{k_{T_v}(T_v = 1000\,K, T_{kin} = 300\,K)} = 40$$

[Polak L.S. (1971)]:

$$\frac{k_{R_{Arrenius}}(T_v = 300\,K, T_{kin} = 6000\,K)}{k_{R_{Arrenius}}(T_v = 300\,K, T_{kin} = 1000\,K)} = 60$$

Русанов В.Д., Фридман А.А. Физика химически активной плазмы. Москва: Наука, 1984.- 416 стр.

$$k_{R_{Arrenius}}(E_v) = k_0 \exp[(-\frac{E_a - \alpha E_v}{T_{kin}})\Theta(E_a - \alpha E_v)$$

$\Theta(E_a - \alpha E_v)$ **- Havisaid function**

α – operating ratio of vibrational energy

Types of reactions	**α**
Endothermic	0,9-1,0
Thermoneutral	0,3-0,6
Exothermic	0,2-0,4