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Decomposition of VOCs with the use of electric discharges

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Plan of the presentation

Introduction

Results

dielectric barrier discharge

spark discharge

Summary and Conclusions

Introduction

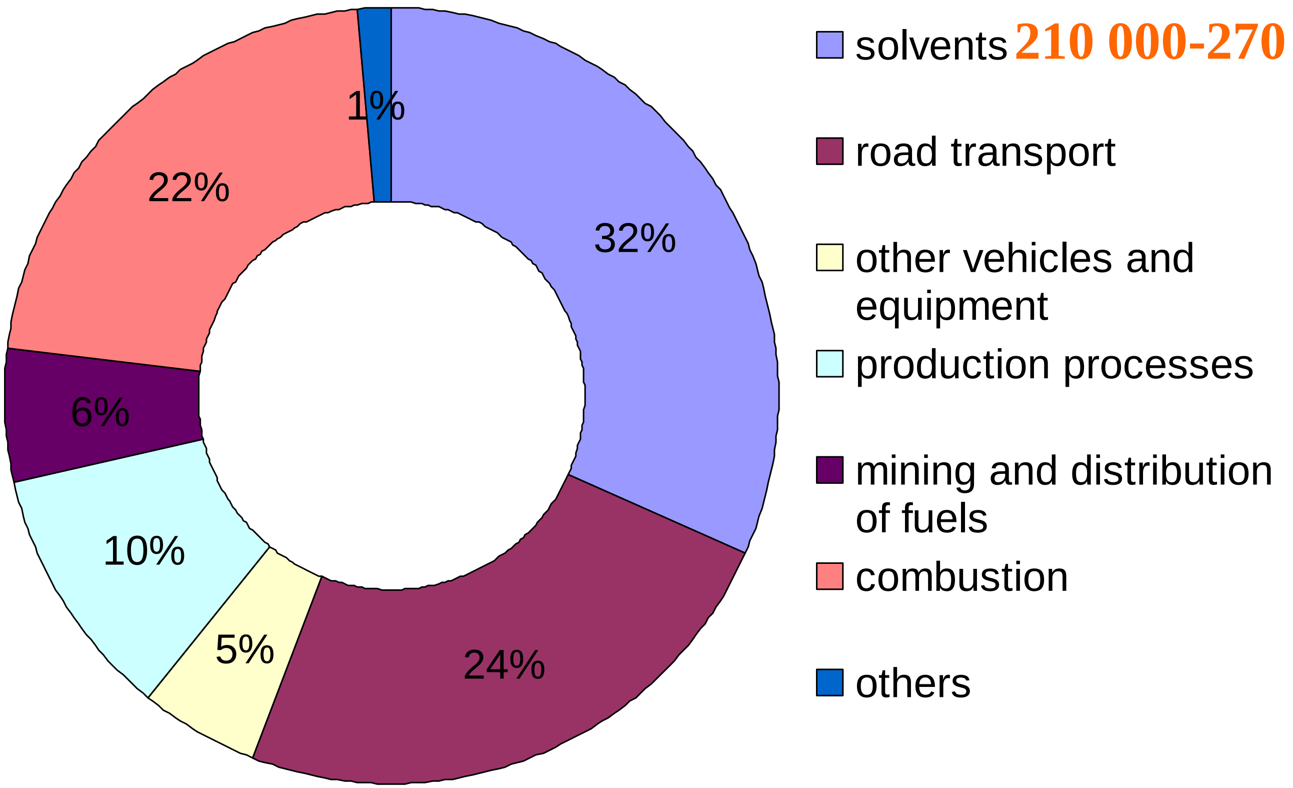
Many groups of compounds include volatile organic compounds:

- ✓ aliphatic hydrocarbons,
- ✓ cyclic hydrocarbons,
- ✓ aromatic hydrocarbons,
- ✓ halocarbons,
- ✓ alcohols,
- ✓ phenols,
- ✓ carboxylic acids,
- ✓ esters ,
- ✓ amines,
- ✓ ethers.

Introduction

Sources of VOC emissions

Total emission ~600 000 t/y



solvents 210 000-270 000 t/y

The National Report Emissions Balance of SO_2, NO_x, CO, NMVOCs, NH_3, dust, heavy metals and POPs for the years 2009-2010 in the system of classification SNAP and NFR , 2012
Environment, Central Statistical Office, 2011

Introduction

Estimated VOCs emissions from the use of solvents in 2030 will to 230 000 t.

Studies of VOCs decomposition are performed because these substances:

- contribute to the greenhouse effect,
- are harmful to health.

Halogenated hydrocarbons emissions are ~ 7 million tones (as CO_2 equivalents)

Fifth National Communication to the Conference of Parties to the UN Framework Convention on Climate Change, IEP and ME, 2010

Environment, Central Statistical Office, 2011

Methods for reducing VOC emissions:

Condensation → regeneration
high concentration

Combustion → large and steady steam
2000-3000 €/kg

Plasma → low concentration
periodic operation

Introduction

At the Faculty of Chemistry of Warsaw University of Technology, processes occurring in the following discharges are studied:

Glid-Arc Discharge

- K. Krawczyk, B. Ulejczyk, Influence of water vapor in CCl_4 and $CHCl_3$ conversion in gliding discharges, *Plasma Chem. Plasma Process.*, 24, 155-167 (2004)
- K. Krawczyk, B. Ulejczyk, Decomposition of chloromethanes in gliding discharges, *Plasma Chem. Plasma Process.*, 23, 265-281(2003)
- K. Krawczyk, B.Ulejczyk, H.K. Song, A. Lamenta, B. Paluch, K. Schmidt-Szałowski, Plasma-catalytic reactor for decomposition of chlorinated hydrocarbon, *Plasma Chem. Plasma Process.*, 29, 27-41 (2009)

Introduction

Spark Discharge

•K. Krawczyk, S. Jodzis, A. Lamenta, K. Kostka, B. Ulejczyk, K. Schmidt-Szałowski, Carbon Tetrachloride Decomposition by Pulsed Spark Discharges in Oxidative and Nonoxidative Conditions, *IEEE T. Plasma Sci.*, 39, 3203-3210 (2011)

•A. Lamenta, S. Jodzis, K. Krawczyk, K. Schmidt-Szałowski**,** Carbon tetrachloride decomposition in spark discharge plasma, *Pol. J. Chem.*, 83, 169-174 (2009)

Dielectric Barrier Discharge

- B. Ulejczyk, K. Krawczyk, M. Młotek, K. Schmidt-Szałowski, Ł. Nogal, B. Kuca, Decomposition of carbon tetrachloride in the reactor of dielectric barrier discharge with different power supplies, *Eur. Phys. J. Appl. Phys.*, 61, 24324p1-24324p7 (2013)
- K. Schmidt-Szałowski, K. Krawczyk, J. Sentek, B. Ulejczyk, A. Górska, M. Młotek, Hybrid plasma-catalytic systems for converting substances of high stability, greenhouse gases, *Chem. Eng. Res. Design*, 89, 2643-2651 (2011)

Dielectric barrier discharge

Process parameters:

- Gas flow rate – 5, 10, 20, 30 Nl/h
- VOCs – CCl_4, $CHCl_3$, C_2HCl_3
- VOCs concentration – 0.1, 0.34%
- Air - synthetic (H_2O<10 ppm), atmospheric dry (H_2O=20 ppm), atmospheric wet (H_2O=0.4%)

Specific energy – energy referenced to total gas

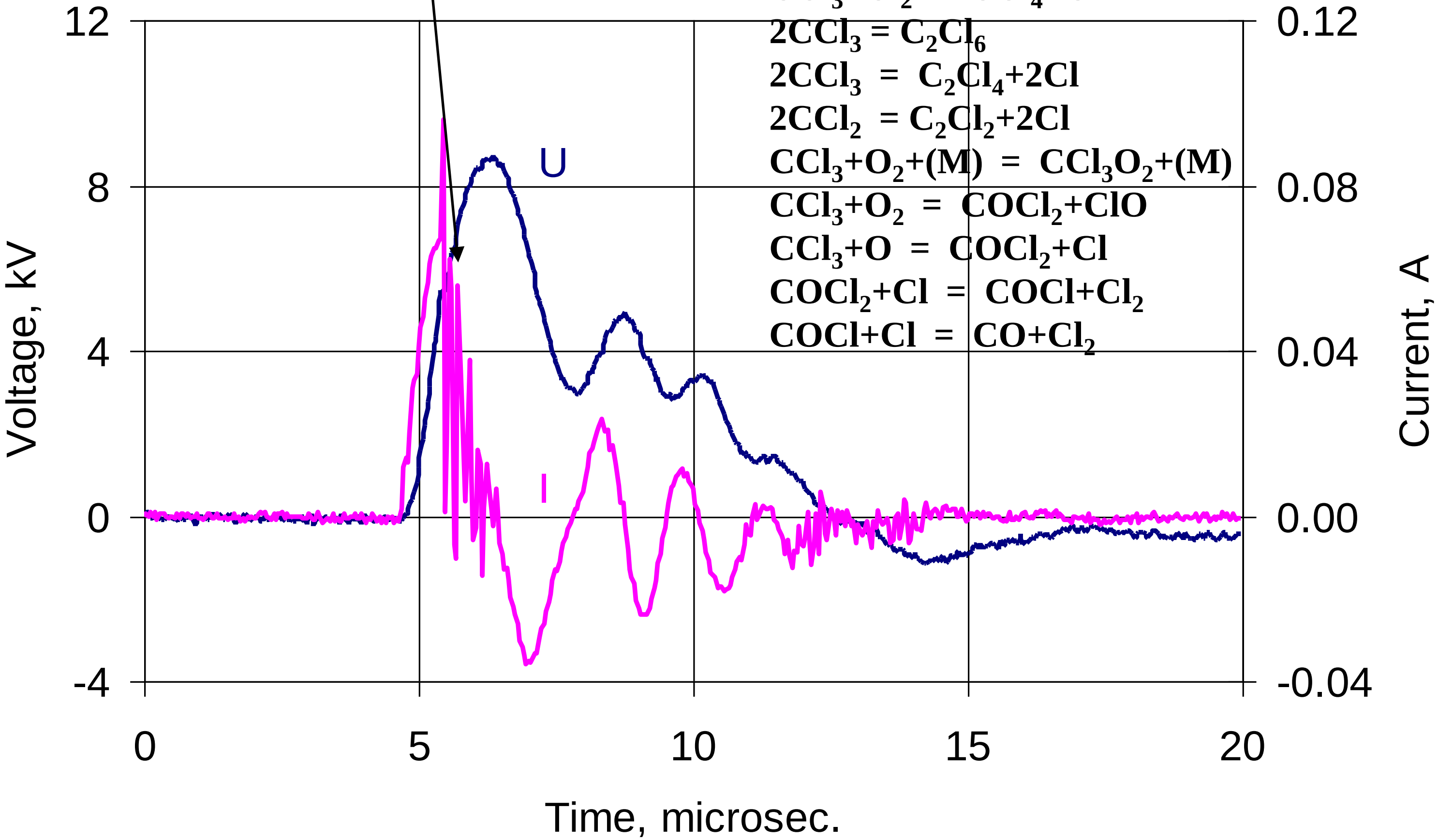
Energy consumption – energy referenced to converted pollutans

Two types of pulsed power supply systems were used to generate the dielectric barrier discharge.

Traces of voltage and current

$CCl_4 + e = CCl_3 + Cl^-$
$CCl_4 + e = CCl_3 + Cl + e$
$O_2 + e = O + O + e$

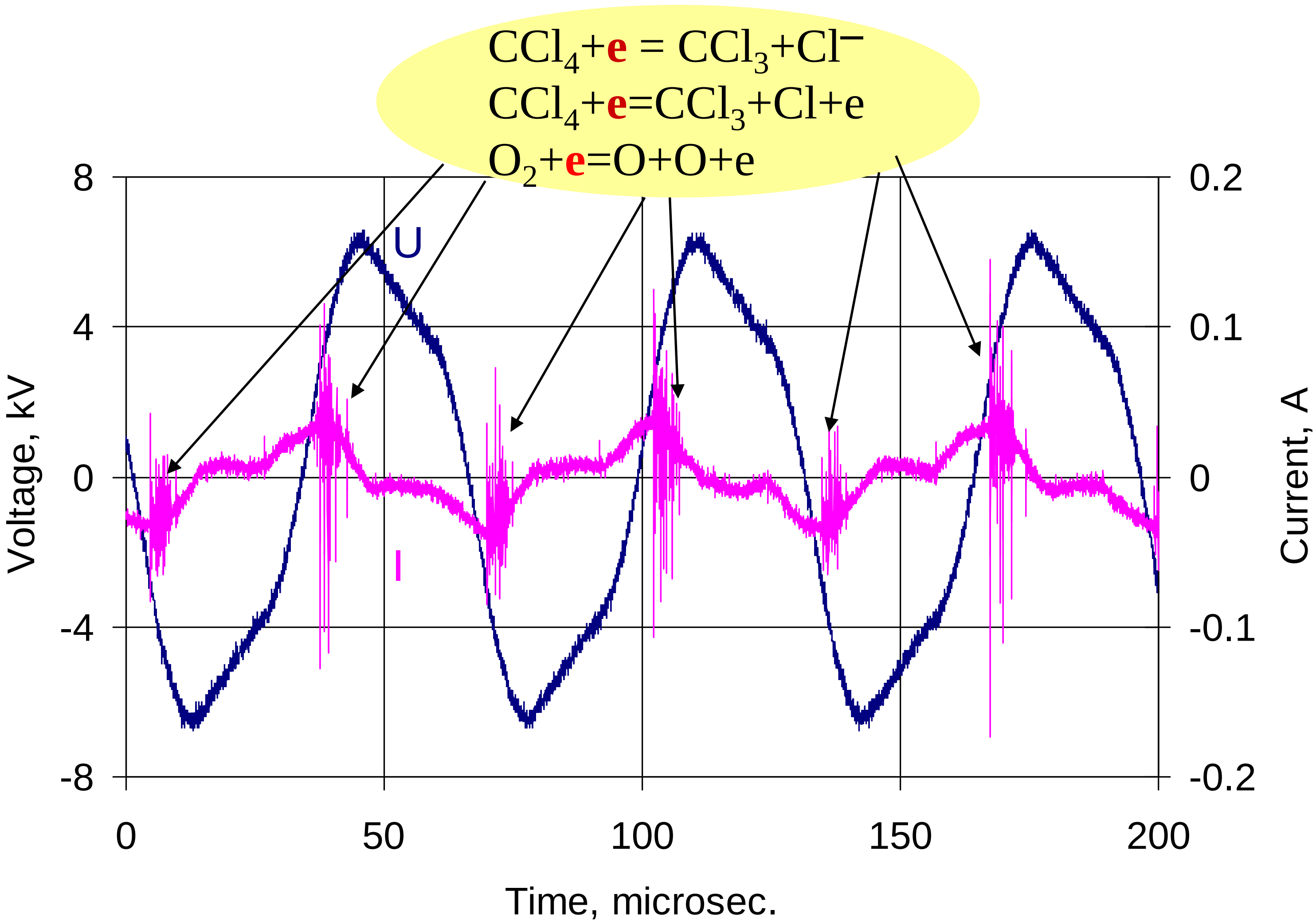
$CCl_4 + Cl = CCl_3 + Cl_2$
$O + CCl_4 = CCl_3 + ClO$
$CCl_3 + Cl + (M) = CCl_4 + (M)$
$CCl_3 + Cl_2 = CCl_4 + Cl$
$2CCl_3 = C_2Cl_6$
$2CCl_3 = C_2Cl_4 + 2Cl$
$2CCl_2 = C_2Cl_2 + 2Cl$
$CCl_3 + O_2 + (M) = CCl_3O_2 + (M)$
$CCl_3 + O_2 = COCl_2 + ClO$
$CCl_3 + O = COCl_2 + Cl$
$COCl_2 + Cl = COCl + Cl_2$
$COCl + Cl = CO + Cl_2$



Pulsed power supply system of 150-800 Hz frequency.

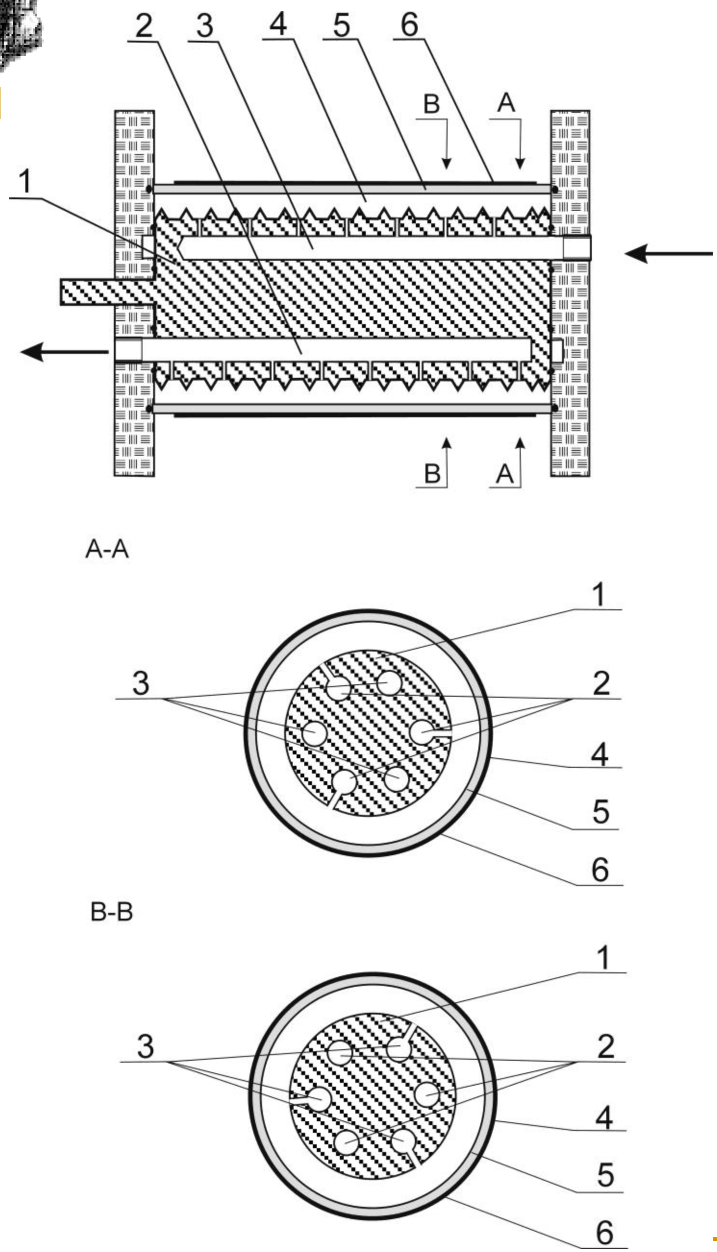
B.M. Penetrante, *Phys. Lett. A*, 209 (2005) 69; K. Krawczyk, *Plasma Chem. Plasma Process.*, 23 (2003) 265; Zh. Bo, *Plasma Chem. Plasma Process.*, 27 (2007) 546; H. Nichipor, *Radiat. Phys. Chem.*, 57 (2000) 519; M. Koch, *Envir. Sci. Technol.*, 29 (1995) 2946; B.M. Penetrante, *Jpn. J. Appl. Phys.*, 36 (1997) 5007; J.V. Michael, *J. Phys. Chem.*, 97 (1993) 1914; A. Indarto, *Plasma Dev. Operat.*, 14 (2006) 1; K.A. Foglein, *Chemosphere*, 50 (2003) 9.

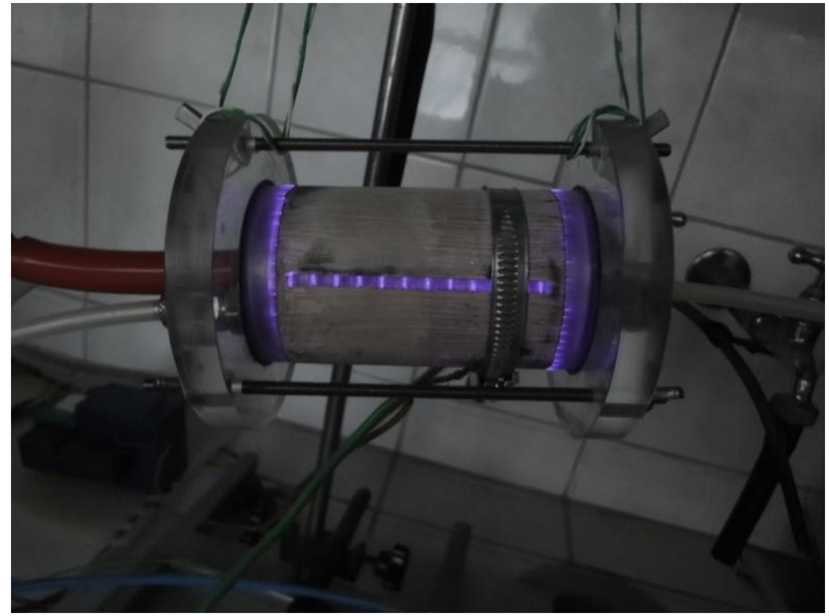
Traces of voltage and current



Pulsed power supply system of 30 kHz frequency and regulated duration of pulse discharge.

Reactor





Schema of the reactor.

1 – high-voltage electrode

2, 3 – internal channels

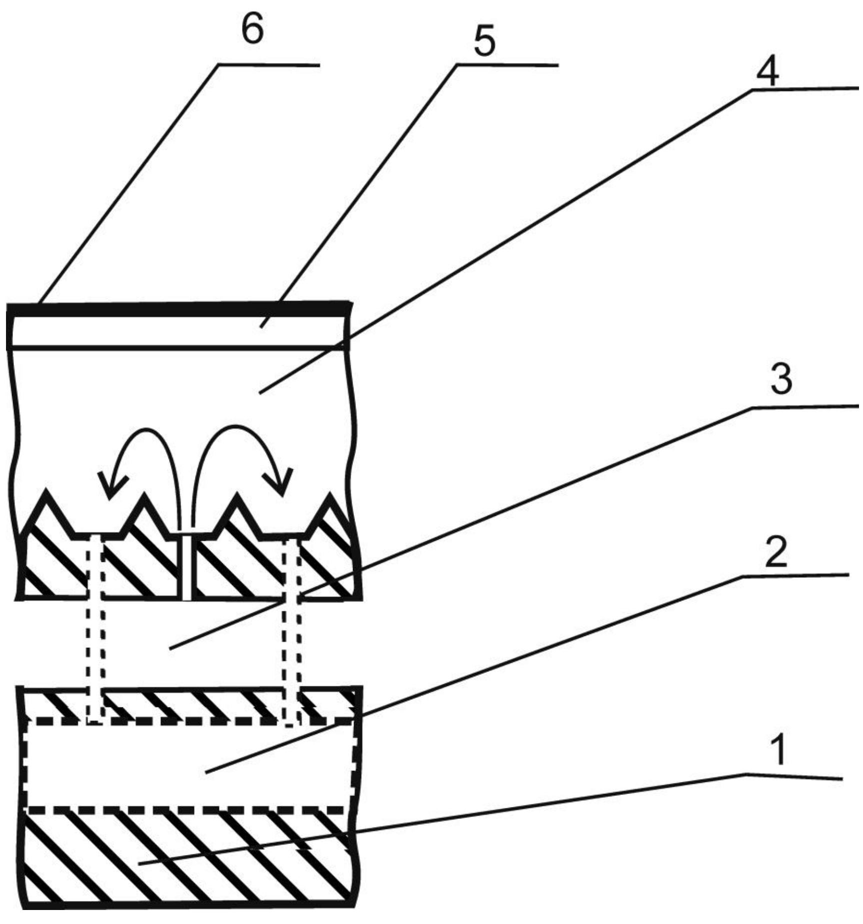
4 – discharge zone

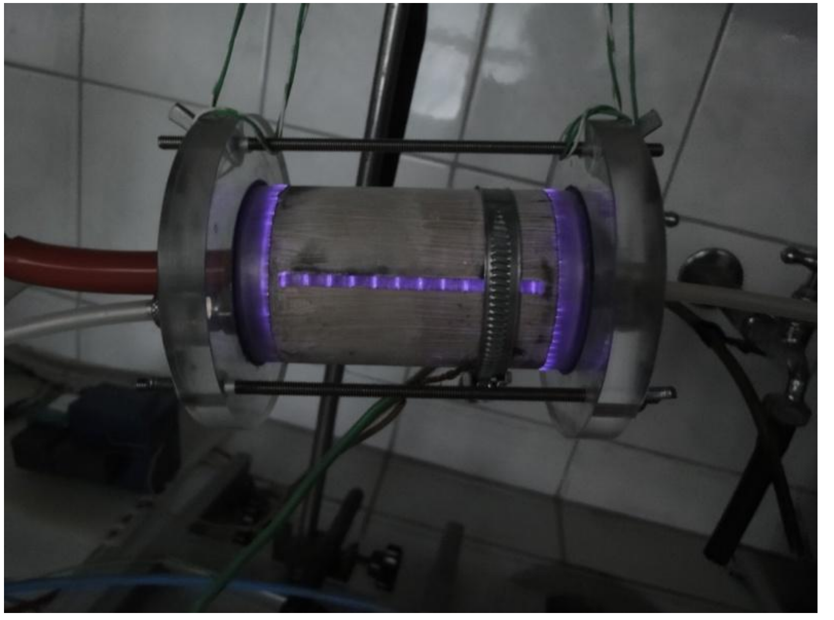
5 – dielectric barrier

6 – grounded electrode

Reactor capacity - 6.9 cm^3

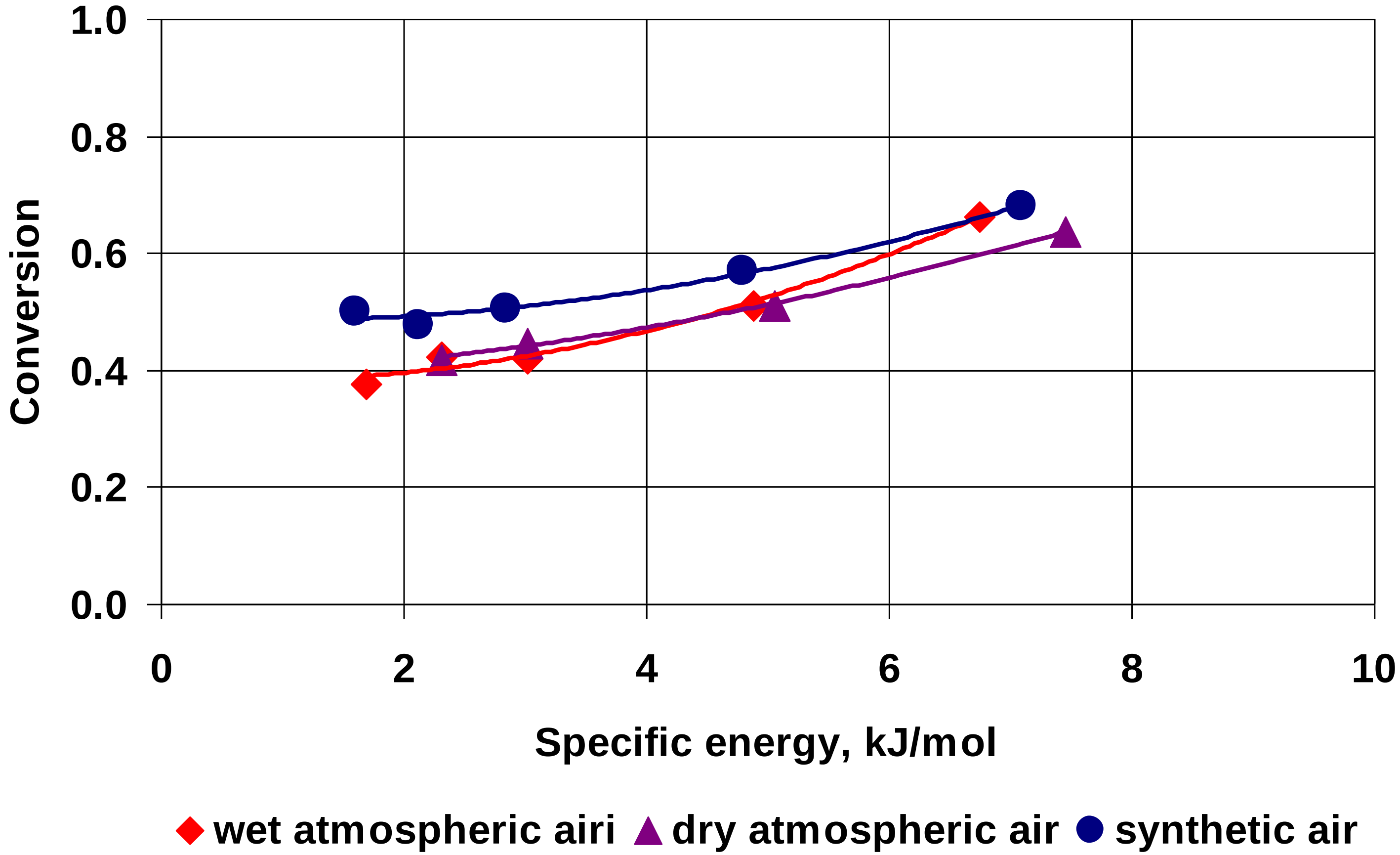
Reactor





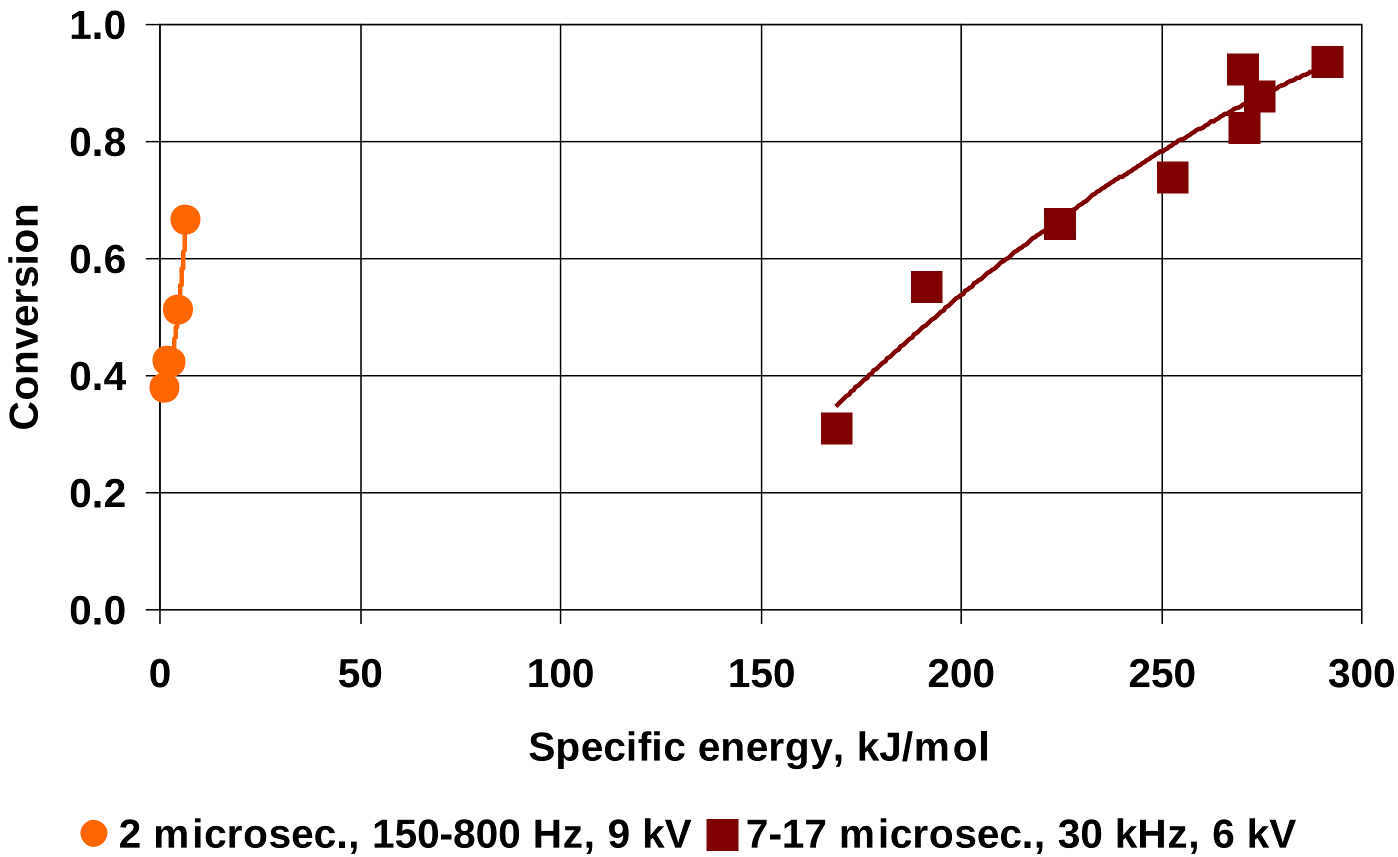
Schema of the reactor.
1 – high-voltage electrode
2, 3 – internal channels
4 – discharge zone
5 – dielectric barrier
6 – grounded electrode

Results



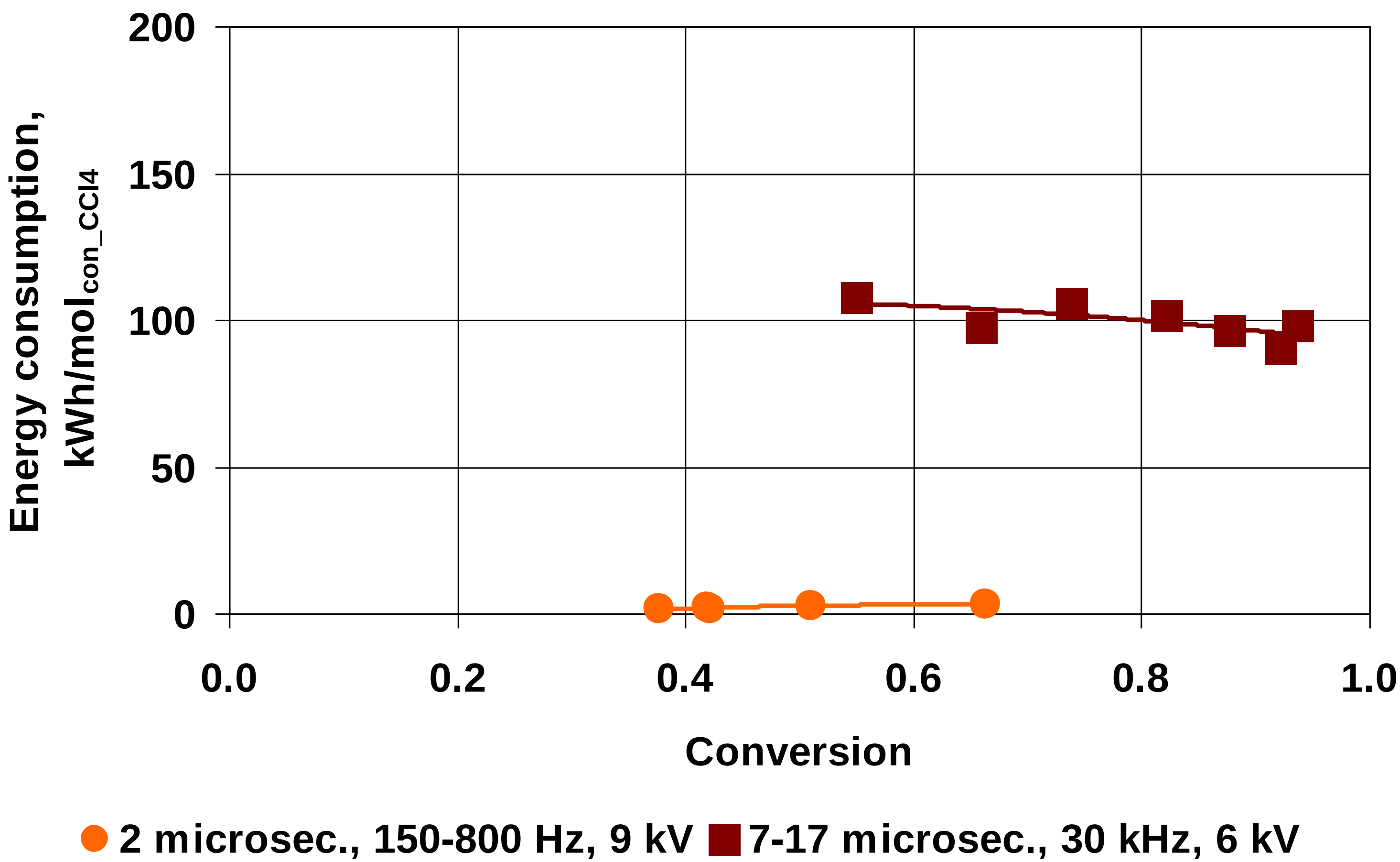
Influence of the type of the treated air on the decomposition of CCl_4.
Gas flow rate 10 Nl/h. CCl_4 concentration 0.1%.

Results



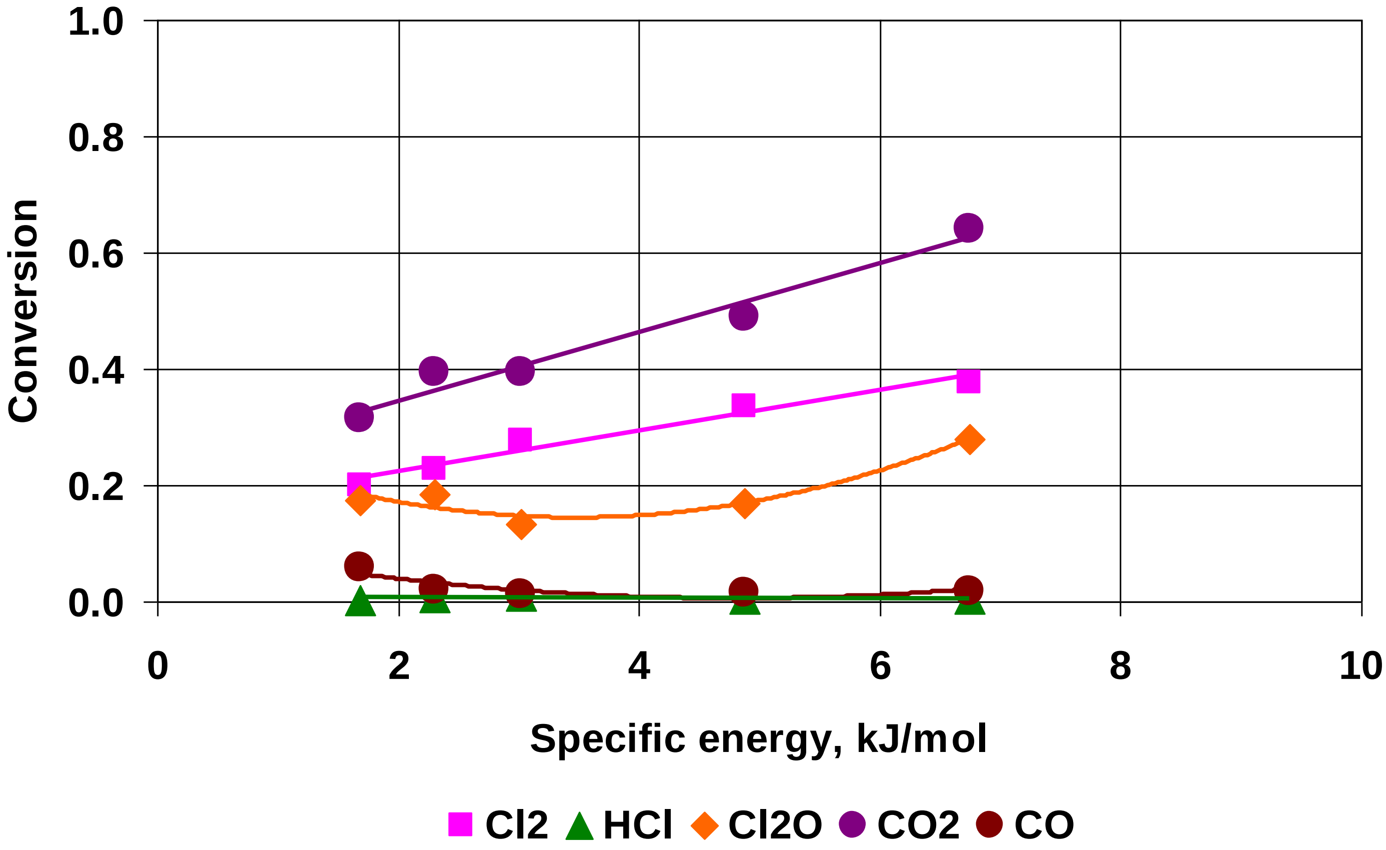
Influence of the type of power supply system on the decomposition of CCl_4.
Gas flow rate 10 Nl/h. CCl_4 concentration 0,1%. Wet atmospheric air.

Results



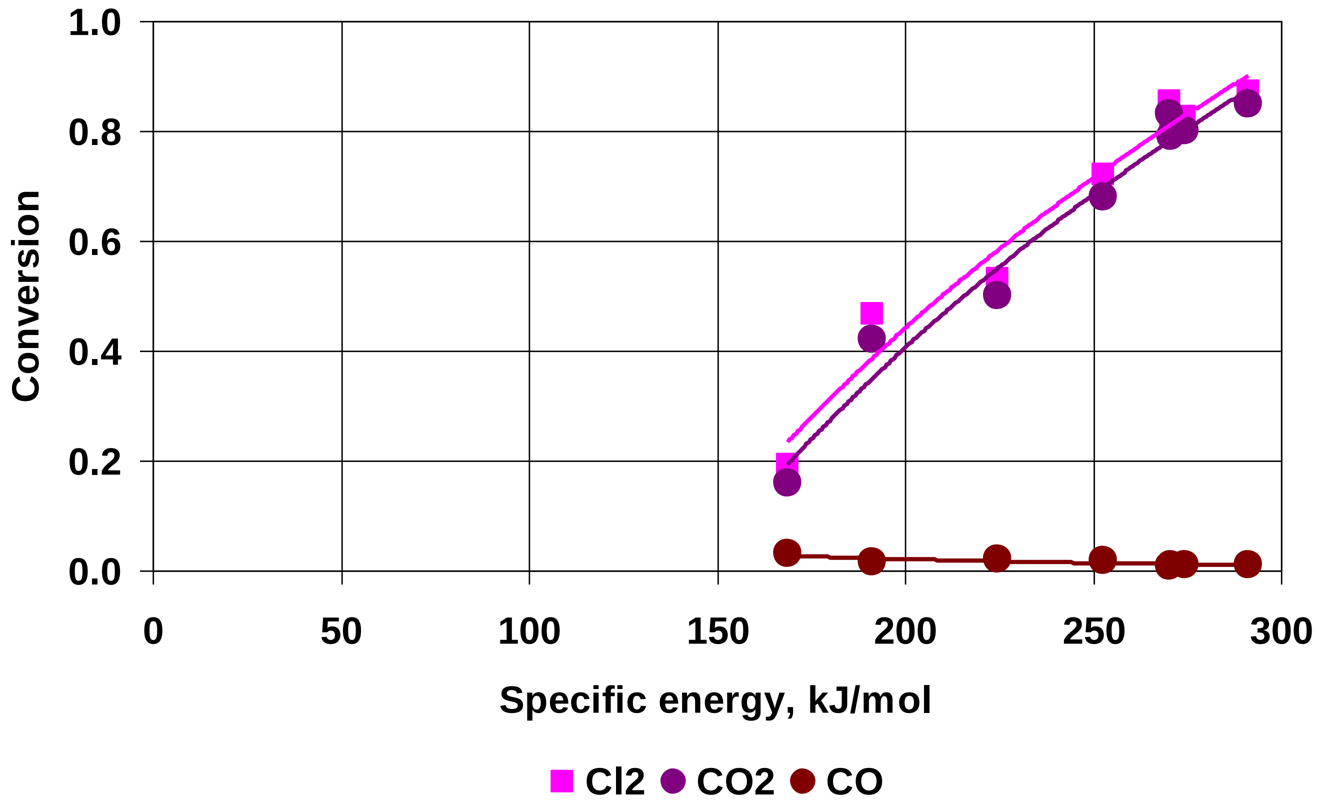
Influence of the type of power supply system on the decomposition of CCl_4. Gas flow rate 10 Nl/h. CCl_4 concentration 0.1%. Wet atmospheric air.

Results



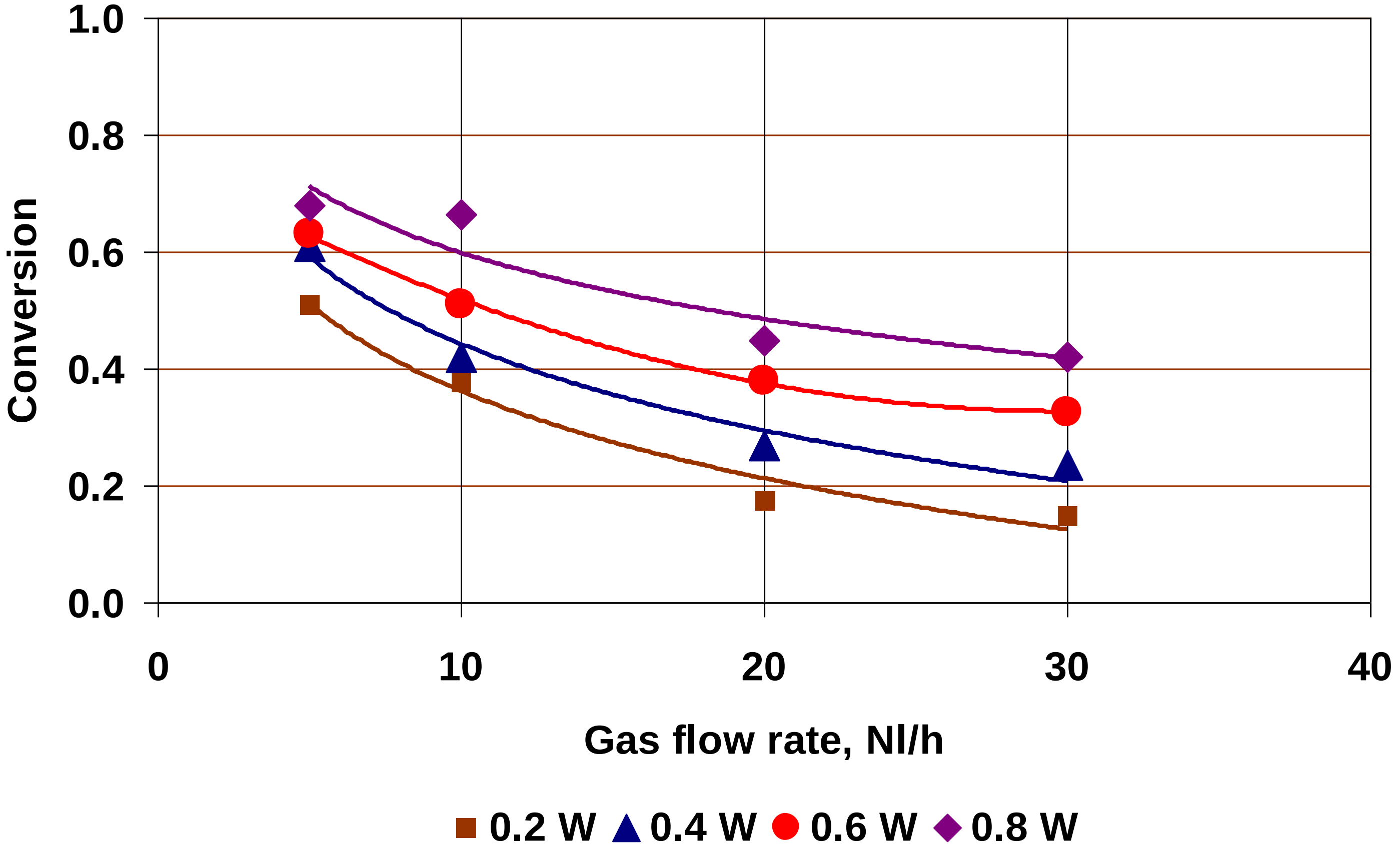
Products of CCl_4 decomposition. Gas flow rate 10 Nl/h. CCl_4 concentration 0.1%. Wet atmospheric air. Pulsed power supply system of 150-800 Hz of frequency, 9 kV of voltage, 2 microseconds of pulse duration.

Results



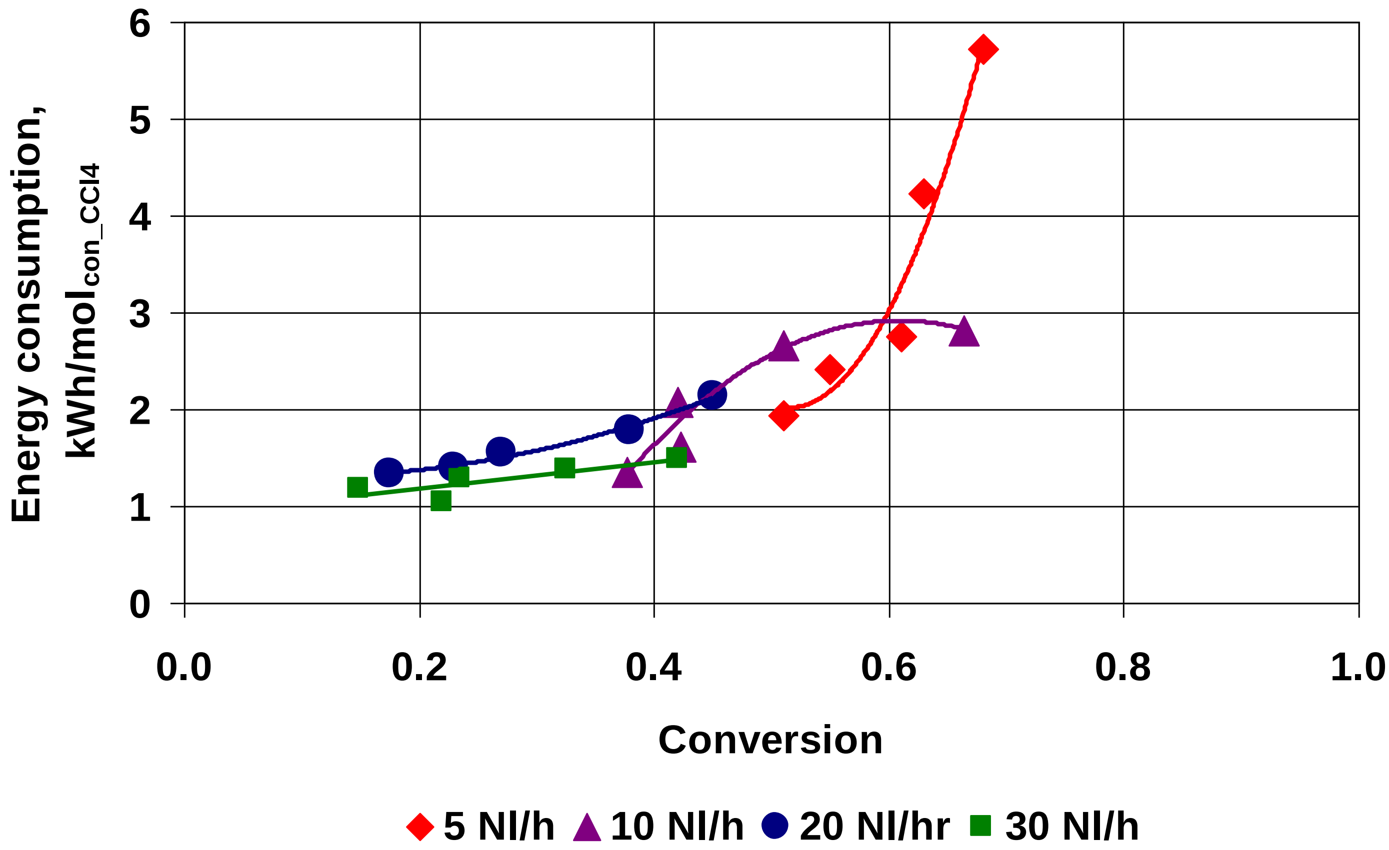
Products of CCl_4 decomposition. Gas flow rate 10 Nl/h. CCl_4 concentration 0.1%. Wet atmospheric air. Pulsed power supply system of 30 kHz of frequency, 6 kV of voltage, 7-17 microseconds of pulse duration.

Results



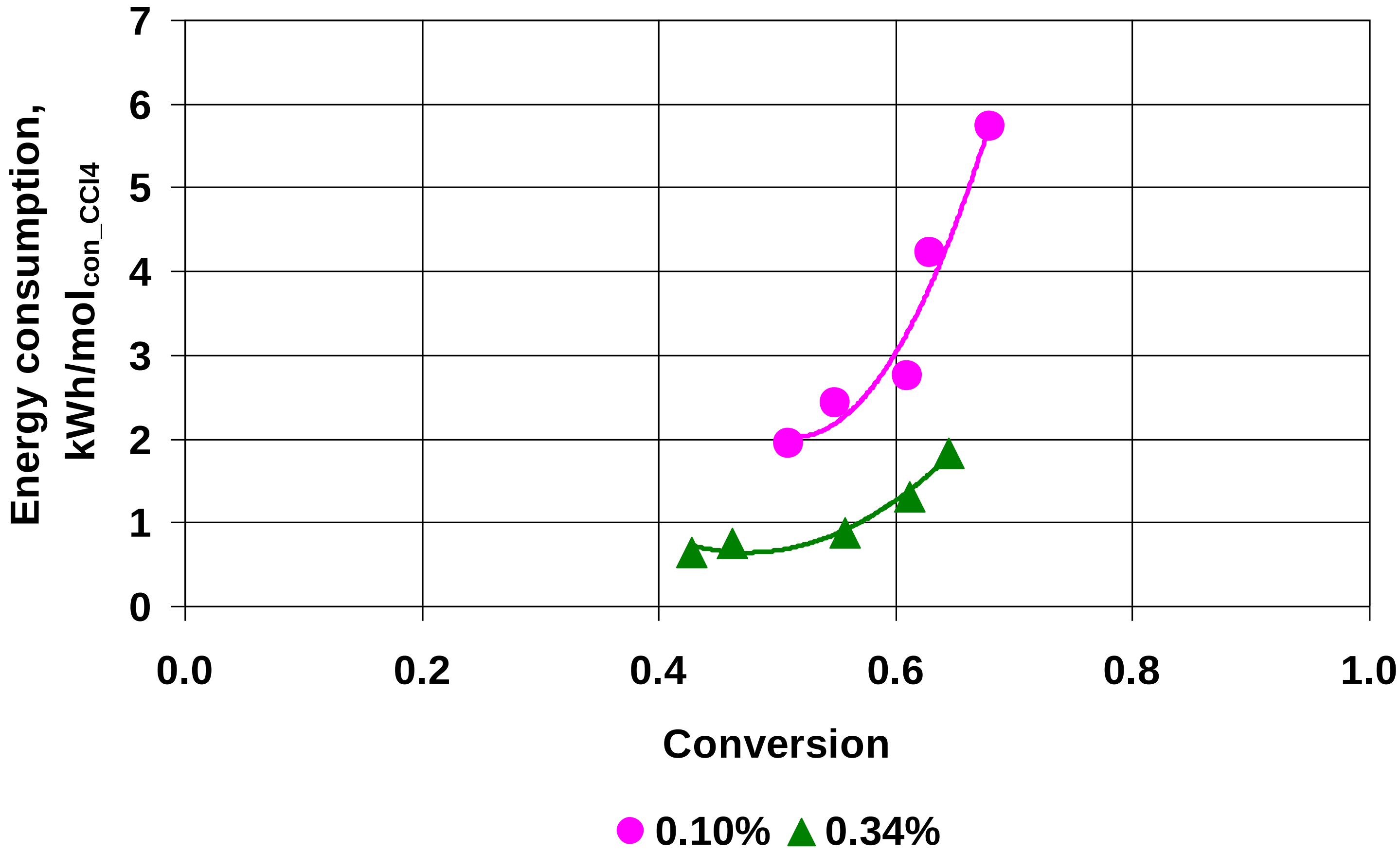
Influence of the gas flow rate on the decomposition of CCl_4.
CCl_4 concentration 0.1%. Wet atmospheric air.

Results



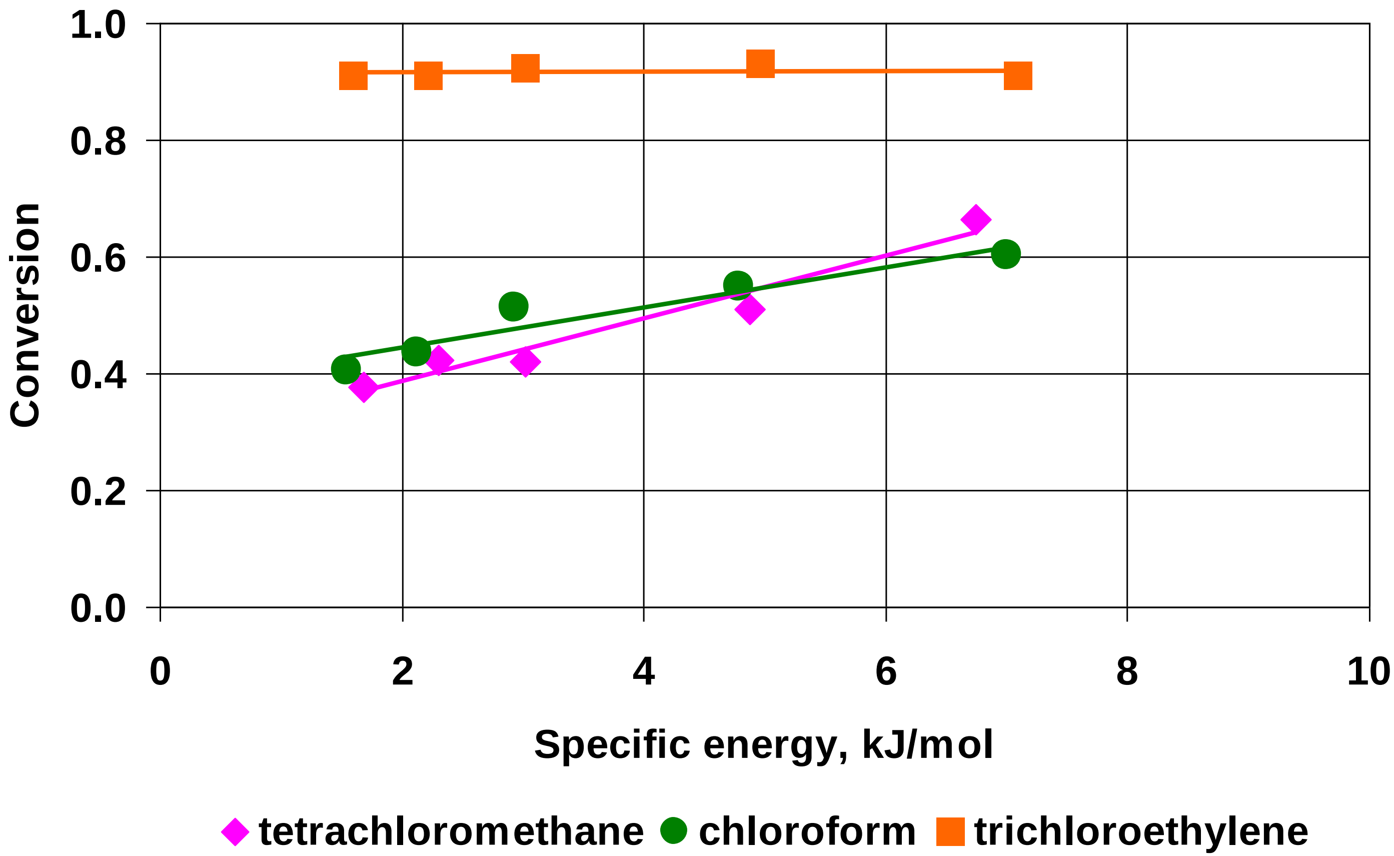
Influence of the gas flow rate on the energy consumption. CCl_4 concentration 0.1%. Wet atmospheric air.

Results



Influence of the initial concentration of CCl_4 in air on energy consumption. Gas flow rate 10 Nl/h. Wet atmospheric air.

Results



Comparison of decomposition processes of different compounds.
Gas flow rate 10 Nl/h. VOCs concentration 0.1%. Wet atmospheric air.

Summary of dielectric barrier discharge

Dielectric barrier discharge can be used for cleaning the air.

Barrier discharge can be operated at:
•different the gas flow rate,
•different concentration of VOCs.

Energy consumption depends on:
•gas flow rate,
•concentration of VOCs,
•power supply system.

Various compouds decomposed with various efficiency.

Composition of the products of VOCs decomposition can be controlled by the type of used power supply system.

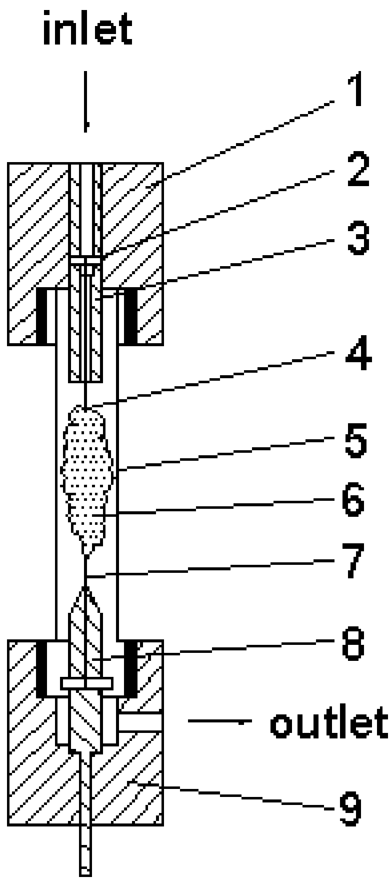
Spark discharge

Process parameters:

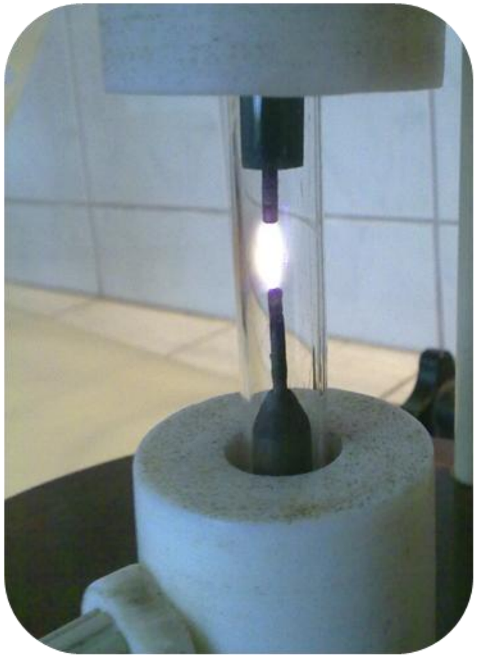
- Gas flow rate – 10 Nl/h
- CCl_4 concentration – 0.1%
- Synthetic air (H_2O<10 ppm)

Two types of pulsed power supply systems were used to generate the spark discharge.

Reactor – spark discharge

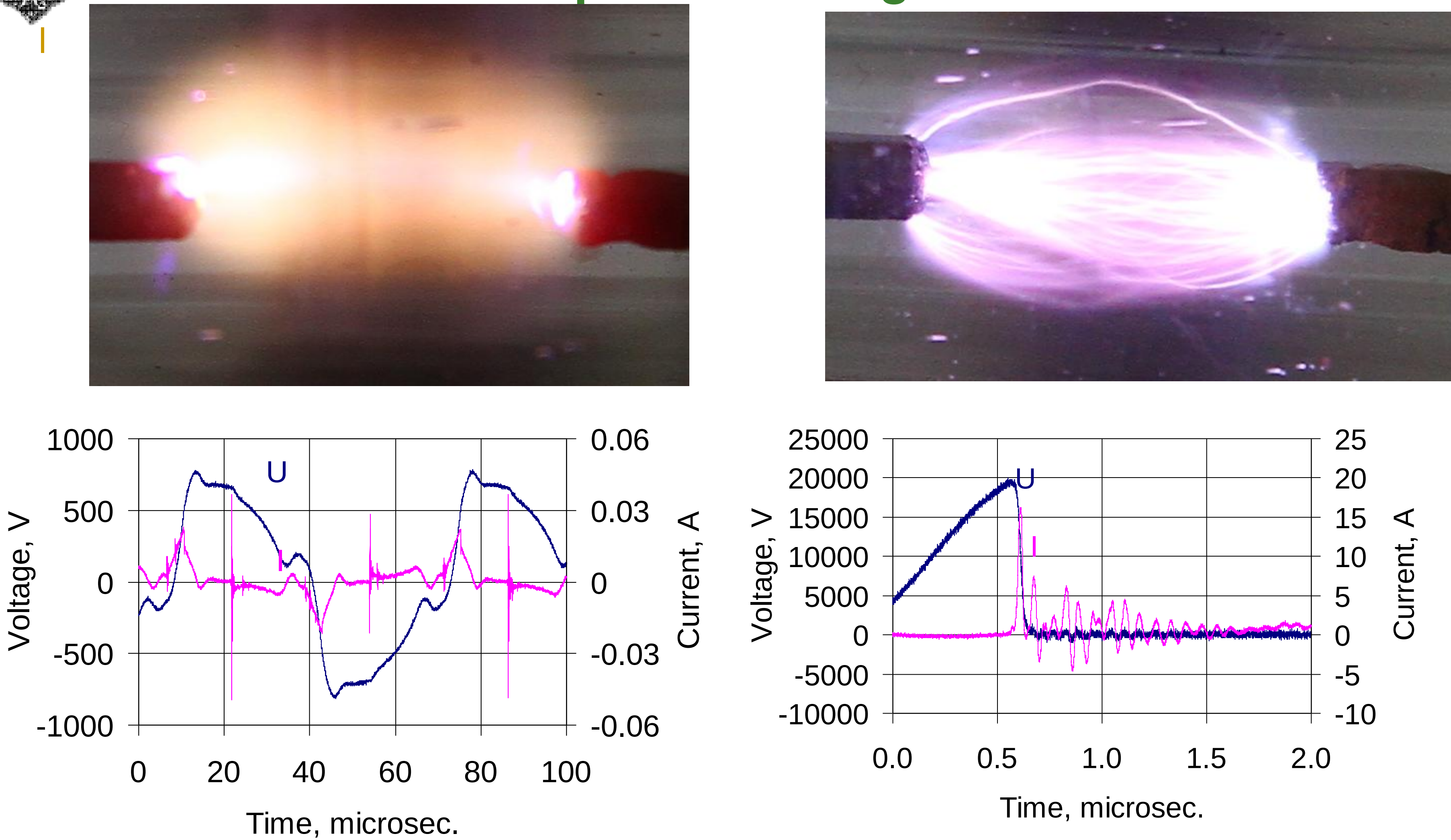


Schema of the reactor.
1,9 - plastic covers
2 - bolts
3,8- stainless steel fence
4,7 - electrode rods
5 - quartz tube
6 - plasma zone



Inner diameter of reactor - 10 mm
Electrodes –2 mm platinium rods
Reactor capacity - 3.6 cm^3
Distance between electrodes – 12 mm

Spark discharge



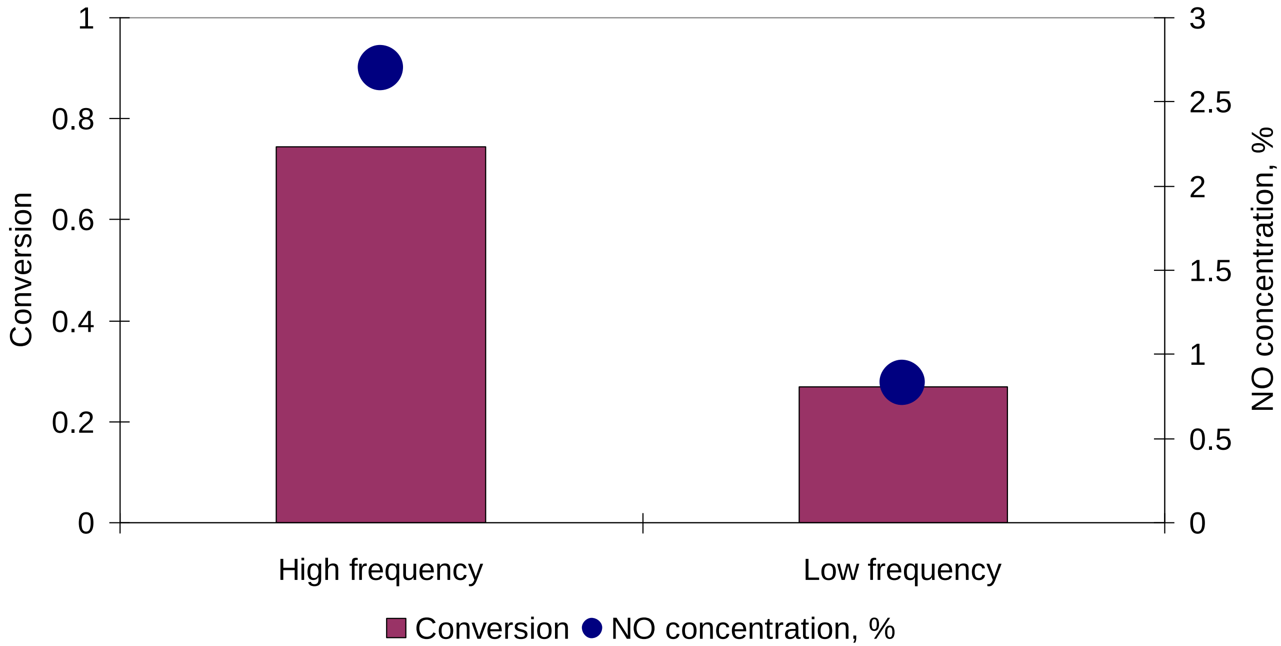
Photos (shutter speed – 1/10 s) and traces of pulses voltage and current of spark discharges powered by various supply power systems.

Spark discharge

30 kHz frequency and 0.8 kV of voltage

210 Hz of frequency and 20 kV of voltage

Influence of type of power supply system on conversion of CCl_4 and NO concentration in outlet gas. Specific energy 8 kJ/mol.

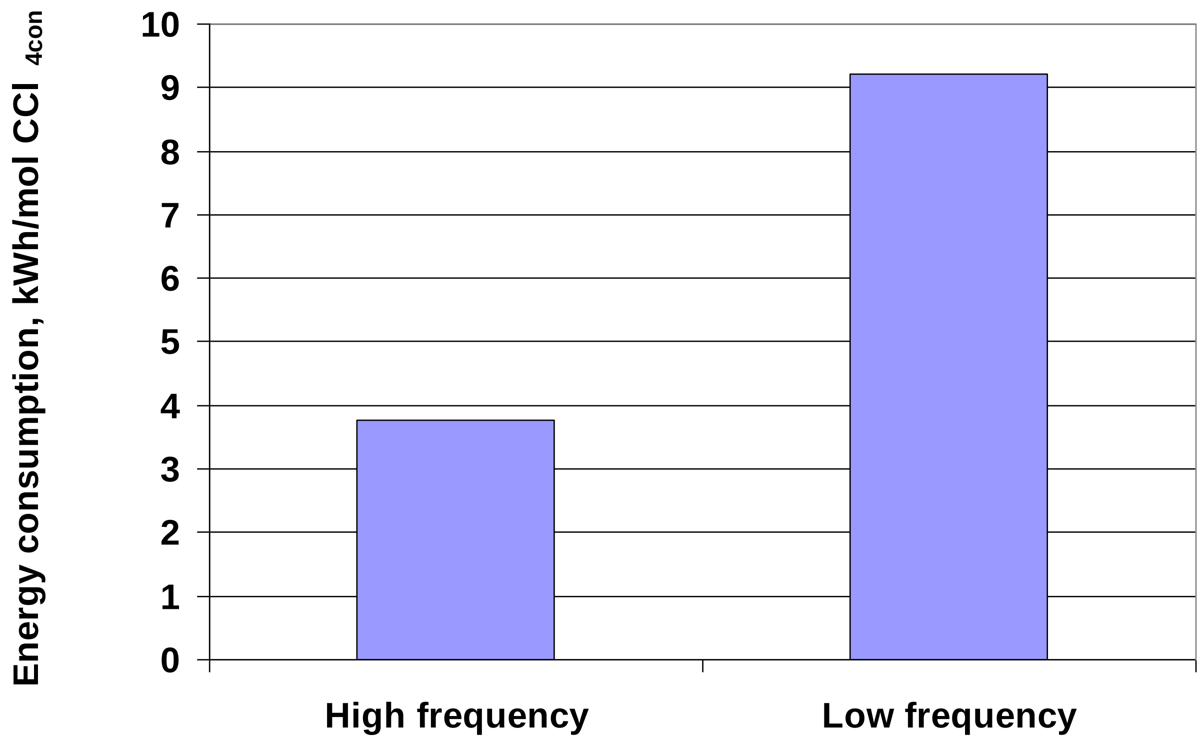


Spark discharge

30 kHz frequency and 0.8 kV of voltage

210 Hz of frequency and 20 kV of voltage

Influence of type of power supply system on energy consumption. Specific energy 8 kJ/mol.



Summary and Conclusions

Dielectric barrier discharge can be used for cleaning the air.
NO is not produced in this discharge.

NO is formed in the spark discharge, for this reason **the spark discharge should not be used to performed the plasma processes in the air**.

Power supply systems influenced on the efficiency of decomposition of contaminants in both studied discharges.
Composition of the products of VOCs decomposition and energy consumption strongly depend on the type of used power supply system.

Plasma process of VOCs decomposition also depends on:
•gas flow rate,
•concentration of VOCs,
•type of contamination.

Acknowledgement

Persons taking participating in the research:

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