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Low-temperature plasma for exhaust gas purification from paint shop - a case study

Abstract. *Devices generating and using non-thermal plasma are often critical parts of industrial set-ups, for purification of exhaust gases. Many research groups work on improvements of plasma generators for ozone (alone or in combination with other oxidants such as H_2O_2, OH radicals, etc.) production. Such oxidants' generators can be successfully applied in the case of "point" gas emissions like chimneys of factories or farms and also for "line" emissions caused by road traffic. Presented work describes plasma generator used for the treatment of factory exhaust gas containing hydrocarbons. Data from plasma burn-up of gas from mold painting factory using gliding arc reactor are presented.*

Streszczenie. *Urządzenia do generowania i zastosowań plazmy niskotemperaturowej są niejednokrotnie ważnymi elementami instalacji przemysłowych do oczyszczania gazów odlotowych. Wiele grup badawczych pracuje nad udoskonaleniem generatorów różnorakich związków utleniających stosowanych do rozkładu polutantów biologiczno-chemicznych. Reaktory plazmowe mogą być używane zarówno w przypadku zanieczyszczeń punktowych takich jak kominy fabryk czy farmy jak też do kontroli zanieczyszczeń liniowych powodowanych przez ruch uliczny. Praca przedstawia generator plazmowy ze ślizgającym się łukiem stosowany do usuwania związków zawierających węglowodory Analizowany jest przypadek plazmowego dopalania gazów odlotowych z lakierni zakładu odlewniczego. (**Plazma niskotemperaturowa do oczyszczania gazów odlotowych z lakierni**)*

Keywords: gliding arc plasma, paint shop exhaust gas, gas treatment
Słowa kluczowe: plazma generowana w ślizgającym się łuku, gazy odlotowe z lakierni, oczyszczanie gazów odlotowych

1. Introduction

Presently, environmental protection is one of the priority topics in the development of industrial societies. Gaseous emissions including sulphurous and nitrous compounds, CO2, ammonia and VOCs become more and more restrictive. Once the Protocol of Göteborg, is fully implemented, Europe's sulphurous emissions should be cut by at least 63%, its NOx emissions by 41%, VOC emissions by 40% and ammonia emissions by 17% compared to 1990 [1, 2]. It is hoped that the rest of the world- especially, highly industrialized countries will also follow this trend in the near future. Usually, the air pollutants are removed from the exhaust air stream via:
-electrostatic precipitators [dust particles],
-water scrubbers or adsorbent filters [gaseous pollutants],
-conversion of pollutants to harmless and/or useful products [3-6].

Among many solutions offered by modern technologies, plasma based technologies are considered promising for removal of pollutants from gases and liquids [7-9]. Low thermal plasma generated at the atmospheric pressure in gliding arc reactors is one of options [10].

Formation of VOCs [Volatile Organic Compounds] during the various stages of technological processes is practically unavoidable. They are generated in many manufacturing procedures in order to obtain final products such as paints, dyes, silicones, tires, detergents, pesticides, fire-proof materials, semiconductors, etc. Among the conventional technologies for eliminating these pollutants there are catalytic oxidation, thermal incineration and carbon adsorption. However, with the VOCs diluted to the concentration less than 1000 ppm, the energy consumption for conventional abatement processes become high [6, 11-12].

Plasma based techniques including low temperature plasma formed in corona and barrier discharge are widely investigated by various research groups: [3,5,13-14].

The best results were obtained in reactors, which construction allowed combination of electrical discharge with other processes for instance the catalyst or ion-beam [14]. Harada et al., proposed novel, high efficiency system integrating surface corona discharge induced plasma and a ceramic filter [15].

There were also attempts to remove polychlorinated VOCs on the example of tetrachloride using atmospheric pressure plasma torch [16].

Gliding arc as a self-state of art for the exhaust gas treatment was proposed over a decade ago by Czernichowski et al., [10].

Regions of thermal and non thermal plasma are formed during the electrical discharge. Up to 80% of the gliding arc power can be dissipated in the non-equilibrium zone and energy may be directly absorbed by endothermic chemical reactions. Very short residence time of reagents in the chamber permits high specific throughputs in the reaction zone, which generally exceed by four orders of magnitude other chemical methods, including electrochemical and thermal ones [17]. The capability to handle high flow rates with high concentration of pollutants is another advantage for industrial applications.

2. GlidArc reactor and experimental set-up

Gliding arc reactor was tested for the decomposition of 0.1–0.5% of aromatic VOCs and 1–8% of chlorinated VOCs diluted in atmospheric air and conversions exceeding 50% were obtained [18]. Purification of water solutions was also possible using gliding arc set-up. Locke at al. confirmed formation of reactive species during the discharge in gas over the pure water [19]. Brisset group made an extensive investigation of pollutants' removal and decolorization in gliding arc reactor [20, 21].

Plasma burn-up of gases emited from factory was tested using pilot-plant set-up installed in foundry's production line. Gases polluted during painting and drying of molds were mixed with hot air and emitted to the atmosphere via 3 chimneys. Average flow rate of gas ranged 2000 m^3/h, temperature at the outlet- was 150 ^oC. Main pollutants were heptane, toluene, xylene, butanol, terpentine, and ethyl acetate. The ratio of pollutants varied in dependence on the used paint.

Schemata of molds' drying system with depicted inlets (I), outlets (O) and plasma reactor is presented in Fig. 1. Painted molds were consequently transported via primary drying unit to main drying tunnel, where hot air was dosed through the I_1-I_3 inlets. Polluted air from the main tunnel was

evacuated through the chimneys O_1-O_3. The pilot plant plasma treatment system was installed on the O_1 outlet.

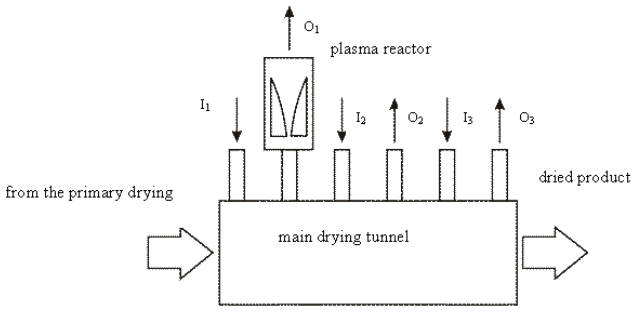


Fig. 1. Schemata of the drying system in the paint shop, (I_1, I_2, I_3)- hot air inlets, (O_1, O_2, O_3)- polluted air outlets.

In the final stage of the project, plasma reactors on all chimneys and PPHARS (post plasma hot air recovery system) are planned. Hot air will be directed back to the main drying tunnel as it is shown in Fig. 2.

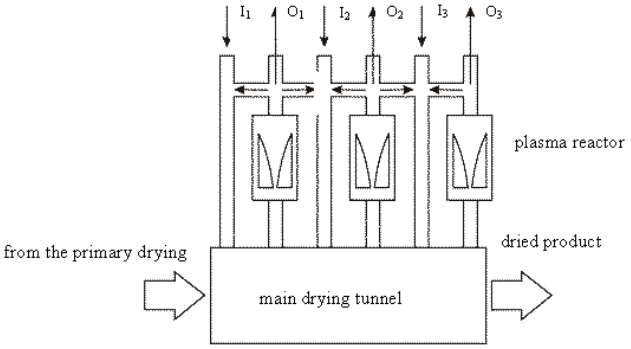


Fig. 2. Schemata of perspective drying system with the hot air recovery.

GlidArc plasma reactor construction is presented in Fig. 3. It consisted of one central ingnition electrode and 3 working electrodes placed around the center of the discharge chamber in 120° distance from each other.

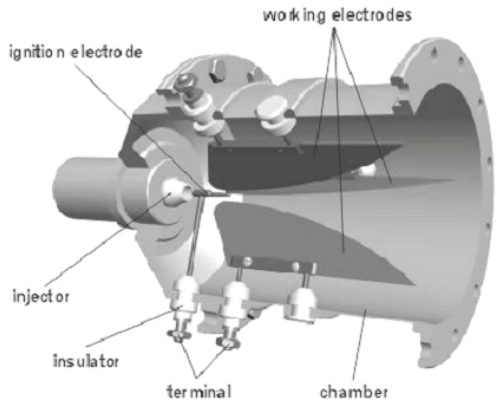
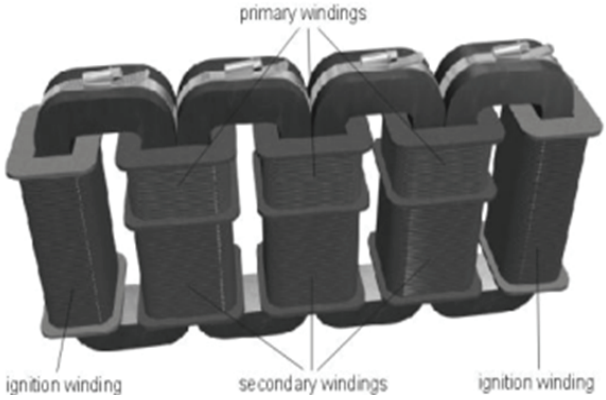


Fig. 3. Gliding arc plasma reactor.

Main parameters of the reactor are summarized in Table 1. GlidArc reactor was powered from the integrated power supply system of parameters described in Table 2, [22-23]. Electric power supply was depicted in Fig. 4.

Table 1. Technical specification of GlidArc reactor.

Height of reaction chamber	500 mm
Diameter of reaction chamber	114 mm
Ignition electrode material	Tungsten ∅ 1 mm
Working electrodes material	Acid-proof steel 0H18N
Number of working electrodes	3
Length of working electrodes	210 mm
Distance between electrodes in the ignition zone	5 mm
Distance between electrodes in the quenching zone	50 mm
Gas flow rate	0,5÷20 m^3/h
Substrate gas	Air and post painting vapours mixture



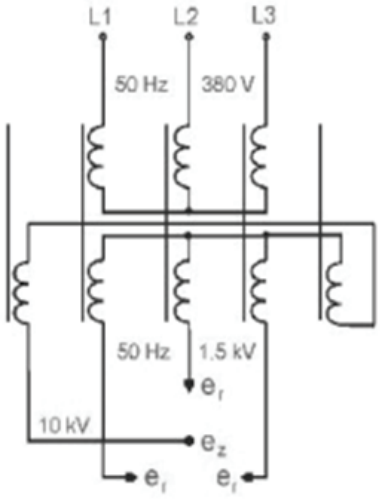


Fig. 4. Electrical power supply (5 limb transformer energizing triple-electrode plasma reactor with the ignition electrode, e_r- working electrodes, e_z- ignition electrode).

Table 2. Specification of power supply set-up.

Voltage (power supply)	400 V, 50 Hz
Voltage (working electrodes)	2 kV, 50 Hz
Current (working electrodes)	2 A
Ignition voltage	10 kV, 150 Hz
Current (ignition electrode)	20 mA

3. Experimental results

Preliminary tests of the reactor were performed in the laboratory conditions using two substrate gases: propane and butane. They tend to mix with air easily. Moreover, simple chemical structure causes difficulties in their removal if model pollutants are highly diluted in air. Experiments were performed at two different chemical mixtures and two different gas flows with the constant input power. The

results of experiments are summarized in Table 3. Indicators SEI and SER depict the usage of electrical energy in the set-up in dependence on the treated gas volume and the mass of pollutants within the treated gas, respectively.

Table 3. Laboratory scale experimental results.

	PROPANE		BUTANE	
Initial concentration (volume), %	1,26	0,48	0,85	0,345
Abatement level %	54	22	47	19
Flow rate, m^3/h	74	88	75	87
Active power, kW	4,3	3,8	4,2	4,1
Gas temperature (inlet), ºC,	25	22	28	28
Gas temperature (outlet) , ºC	410	188	400	210
SEI kWh/m3	0,057	0,044	0,056	0,047
SER kWh/kg	4,3	21	5,4	28

Table 4a. Gas chromatography results before plasma treatment.

Chemical compound	Measurement 1		Measurement 2	
	Retention time	Amount of pollutant	Retention time	Amount of pollutant
	min	%	min	%
methyl ethyl ketone	13,597	0,38	13,705	0,28
ethyl acetate	14,789	13,39	14,865	13,37
1-butanol	18,433	1,09	18,47	1,06
benzene	21,095	10,25	21,114	10,15
heptane	21,318	66,36	21,33	68,10
toluene	21,955	6,32	21,97	6,59
butyl acetate	23,303	0,23	23,315	0,29
ethyl benzene	23,599	0,23	23,614	0,25
xylene	24,423	0,58	24,433	0,61

Table 4b. Gas chromatography results after plasma treatment.

Chemical compound	Measurement 1 - 4 m/s		Measurement 2 - 6 m/s		Measurement 3 - 14 m/s	
	Retention time	Amount of pollutant	Retention time	Amount of pollutant	Retention time	Amount of pollutant
	min	%	min	%	min	%
methyl ethyl ketone	13,778	7,38	13,749	4,7	13,725	5,35
ethyl acetate	14,85	9,2	14,828	8,96	14,809	9,26
1-butanol	18,468	2,14	18,462	1,2	18,452	1,74
benzene	21,116	9,9	21,118	10,47	21,112	10,26
heptane	21,331	62,0	21,338	65,8	21,331	64,56
toluene	21,972	5,7	21,976	6,24	21,97	6,023
butyl acetate	23,318	0,091	23,325	0,057	23,32	0,094
ethyl benzene	23,615	0,16	23,621	0,2	23,615	0,19
xylene	24,44	0,44	24,446	0,53	24,441	0,51

Achieved treatment efficiency is satisfactory and it tends to decrease with the diminishing of the concentration of pollutants in the air mixture. Energy consumption is quite low ranging from 4 to 28 kWh for 1 kg of mineralized hydrocarbons

In the pilot plant installation, concentration of air pollutants was measured using gas chromatography (HP 5890) with thermal desorption unit (Dynatherm Analytical Instruments Inc. model 890). Gas samples for various working gas velocities (4, 6, 14 m/s) were collected just before and after plasma treatment and concentrations of methyl ethyl ketone (butanone), ethyl acetate, 1-butanol, benzene, heptane, toluene, butyl acetate, ethyl benzene, m xylene, o xylene were measured. Results of experiment are presented in Tables 4a, b with the retention time and the amount of certain chemical pollutant given in % (value related to total amount of pollutants in the sample).

Investigated gas consisted of approximately 13% ethyl acetate, 10% benzene, 65% heptane, 6% toluene, 1% 1-butanol and less than 0,5 % of other chemical compounds on average.

The clear decrease in pollutants' concentration in the exhaust air was observed after the plasma treatment. The exception was butanone with the concentration increasing from 0,38% to 5%, or even to 9,7% at 19 m/s of gas velocity.

4. Conclusions

Pilot installation for paint shop exhaust gas plasma treatment was designed and constructed. Pollutants were partly removed from the exhaust gas stream enabling hot air recovery in the future. The energetic efficiency of the process was considered sufficient and in a good accordance with literature data.

Pollutants' concentration was much below the ignition level, what assured the safety of applied solution.

No signs of electrodes' corrosion were noticed during the treatment procedure.

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