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Efficiency Assessment of Using Flammable Compounds from Water Treatment and Methanol Production Waste for Plasma Synthesis of Iron-Containing Pigments

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Abstract. This article describes the possibility of applying the low-temperature plasma for obtaining iron-containing pigments from water purification and flammable methanol production waste. In this paper were calculated combustion parameters of water-saltorganic compositions (WSOC) with different consists. Authors determined the modes of energy-efficient processing of the previously mentioned waste in an air plasma. Having considered the obtained results there were carried out experiments with flammable dispersed water-saltorganic compositions on laboratory plasma stand. All the experimental results are confirmed by calculations.

1. Introduction

Water pollution which caused by the industrial development is a problem of modern society. Conventional water treatment technologies are using chemicals, which makes the process expensive [1,2]. Nonthermal plasma found applicability in various field such as sterilization [3], cancer cell control [4], surface treatment [5], air treatment [6] and biomedical applications [7] due to high performance and low cost [8-10]. When considering the implementation of the technology, a small power supply will be required [2,11].

Scientific and technical progress is intended to improve the quality of human life and to protect people from the many natural and anthropogenic factors, but an inevitable consequence of this progress is rapidly increasing negative impact on the environment. Industrial waste is one of those factors. On the other hand, polluting wastes may be used in industry and usage of them is economically profitable [12].

Tomsk underground water intake (city of Tomsk, Russia) annually produces after water treatment about 3000 tons of water purification waste (WPW) in form of precipitates having following consist [13,14]: Fe (30.3 %), Mn (4.5 %), Si (4 %), Ca (1 %), Mg (0.26 %), Al (0.1 %), Cu (0.05 %) and H_2O (all the rest, ≈ 60 %).

A similar problem is at the wastewater treatment plants of many other localities in different countries all over the world where population uses underground water with high iron and manganese content. It should be noted, that at some regions (for example in China) underground water is the only source of unleavened water and that is why its purification is the special task [15].

Nowadays, actual problem is energy-efficient and environmentally safe obtaining of iron-containing pigments from WPW and wide application of them in the metallurgy (iron-containing raw), in the manufacture of paving slabs, curbs, decorative tiles, glass composite materials, heat-resistant and protective coatings, etc. [16].

However, conventional thermal methods of obtaining pigments from precipitations require significant energy and labor costs.

A significant reduction of energy consumption for the process can be achieved using plasma recycling. In this case precipitations undergo recycling in form of inflammable water-saltorganic compositions (WSOC) with optimal consist having adiabatic combustion temperature about 1200 °C [17].

Thus it is of interest to apply direct plasma obtaining of pigments from WPW for different purposes.

2. Calculation of combustion parameters of WSOC consist of WPW

Tomsk Company «Sibmethachim» occupies a leading position in Russia in the methanol production. It produces about 800 000 tons annually. At the same time it produces about 3 500 tons of inflammable methanol production waste (MPW) consisting of: CH_3OH (50–70 %);
C_2H_5OH (2.6–5.3 %); C_3H_7OH and other higher alcohols (2.5–4.7 %) and H_2O (all the rest percentage) [18].

In present those waste is burned and emitted into the atmosphere. Such MPW utilization technology is environmentally unsafe and leads to a significant loss of thermal energy.

That is why it is of interest to jointly recycle WPW and inflammable component (in this case MPW) in air plasma in forms of WOC. It should be noted that MPW provides more efficient recycling of these wastes.

Liquid combustible compositions are compositions with a net calorific value of more than 8.4 MJ/kg [19]. Net calorific value of inflammable composition should calculate as net calorific value of liquid waste Q_l:

$$Q_l = \frac{(100 - W - A)\cdot Q_d}{100} - \frac{2.5W}{100}, [MJ/kg], \quad (1)$$

where Q_d is net calorific value of dry waste [MJ/kg]; W and A are respectively content of water and solids [%]; 2.5 is value of latent heat of vaporization of water at 0 °C [MJ/kg].

That is why it is of interest to jointly recycle WPW and inflammable component (in this case MPW) in air plasma in forms of WSOC. It should be noted that MPW provides more efficient recycling of these wastes.

Recommendation to consider liquid compositions with $Q_l \geq 8.4$ MJ/kg as inflammable is overstated for many industrial compositions containing combustible components with low values of Q_d.

In contrast to the work [19], we proposed a more objective measure of flammability of liquid compositions in the form of an adiabatic combustion temperature Tad:

$$T_{ad} = \frac{Q_l + C_{was}t_{was} + \alpha \vartheta^0_{ox} C_{ox} t_{ox}}{\upsilon C}, [\circ C], \quad (2)$$

where C_{was} is average mass heat capacity of liquid waste [kJ/kg]; t_{was} is temperature of liquid waste [°C]; α is oxidant flow coefficient; ϑ^0_{ox} is theoretical flow of oxidant (air) [m^3/m^3]; C_{ox} is average heat capacity of an oxidizer [kJ/(m^3·°C)]; t_{ox} is temperature of an oxidizer [°C]; υ are combustion gaseous products of inflammable components of liquid waste [m^3/kg]; C is average volumetric heat capacity of combustion products of liquid waste [kJ/(m^3·°C)].

Figure 1 shows influence of content of WPW and MPW on the WSOC adiabatic combustion temperature. WSOC have different consists.

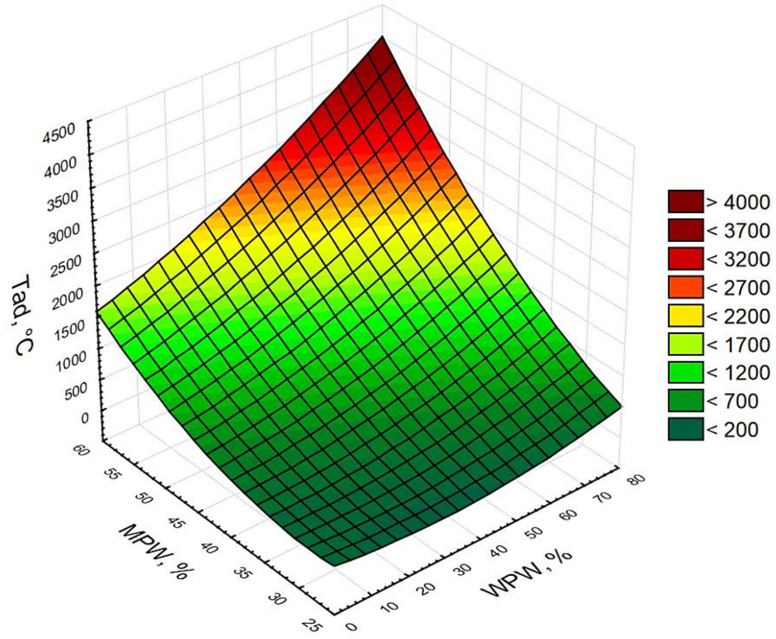

Figure 1. Influence of WPW and MPW content on the WSOC adiabatic combustion temperature

Considering obtained results for practical application may be recommended optimal consist of inflammable WSOC1 (with maximum content of waste): 50% WPW : 50 % MPW.

3. Calculation of equilibrium consists of products formed during WSOC recycling

To determine optimal modes of the plasma recycling there were calculated equilibrium consists of gaseous and condensed products of joint WPW and MPW recycling for recommended (optimal) WSOC 1. Licensed PC program TERRA was used to perform the calculations with following parameters: atmospheric pressure (0.1 MPa), temperature range (300–4000 K), mass fraction range of air heat transfer agent (0.1–0.95).

Figure 2 shows characteristic equilibrium consists of gaseous (a) and condensed (b) products of optimal WSOC1 recycling in plasma. Air mass fraction is 79 %.

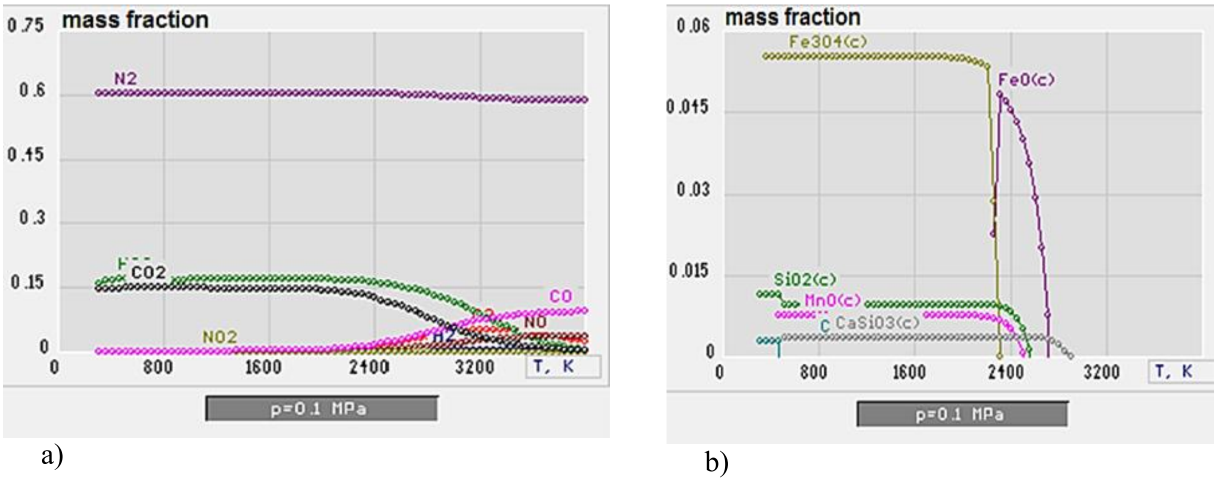

Figure 2. Equilibrium consists of gaseous (a) and condensed (b) products of optimal WSOC1 recycling in plasma (79 % air : 21 % WSOC1)

The analysis of equilibrium consists (figure 2) shows main gaseous products of WSOC1 recycling at temperature lower 1500 K and 79 % of air mass fraction: N_2, H_2O and CO_2. Condensed products include simple and complex metal oxides, comprising magnetic iron oxide Fe_3O_4(c). This fact indicates a possibility to apply magnetic sedimentation. Absence of soot C(c) and insignificant amount of gaseous CO, NO and NO_2 indicates that the plasma recycling of optimal WSOC1 occurs optimally.

Air mass fraction increasing up to 80 % (figure 3) does not influence on consist of gaseous products, but changes consist of condensed ones. The last include simple and complex metal oxides, comprising nonmagnetic iron oxide Fe_2O_3(c).

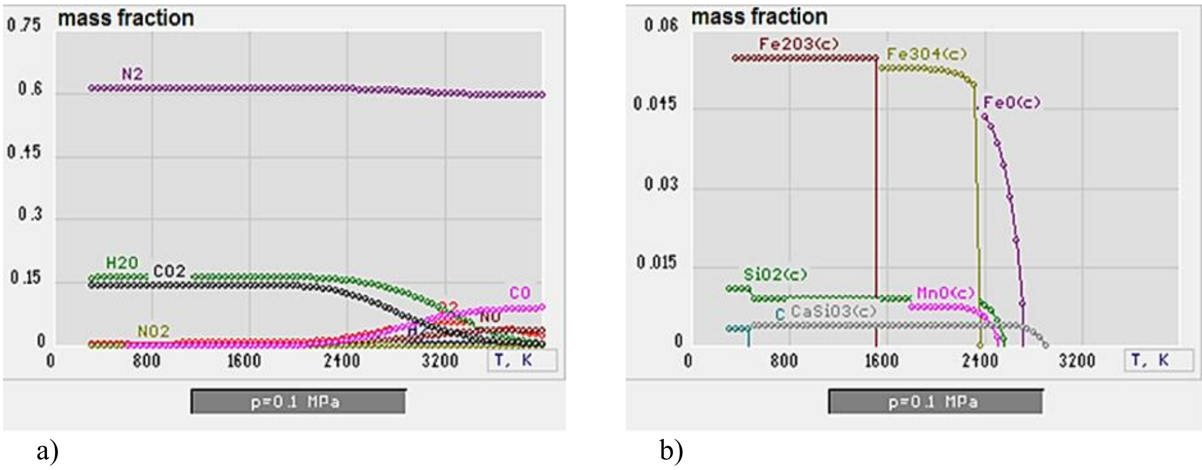

Figure 3. Equilibrium consists of gaseous (a) and condensed (b) products of optimal WSOC recycling in plasma (80 % air : 20 % WSOC1)

Considering obtained results for practical application may be recommended optimal modes of process:

- WSOC consist:50 % WPW : 50 % MPW;
- air mass fraction: 79 % air, 21 %WSOC1;
- temperature range: (1500 ± 100) K.

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4. Experimental confirmation of recommended modes for WPW and MPW recycling in plasma

Plasma stand «Plasma unit on the basis of high-frequency generator VChG 8-60/13-01» was used to experimentally verify recommended process conditions of joint plasma recycling wastes in high-frequency air plasma torch discharge. Figure 4 shows the scheme of this plasma unit.

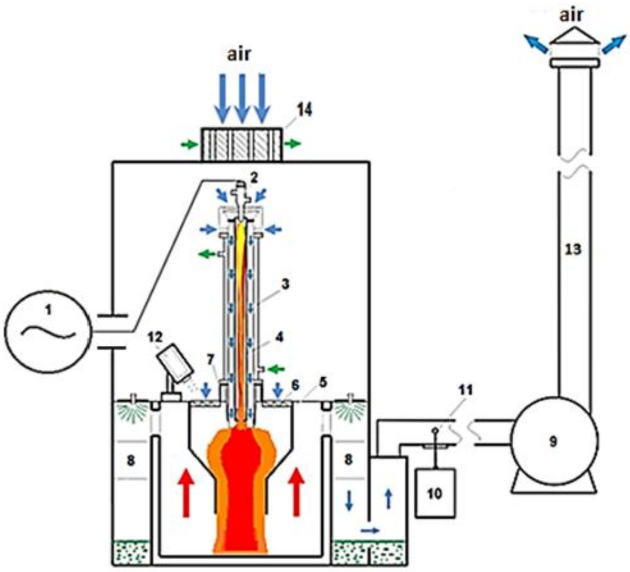

Figure 4. Scheme of laboratory plasma unit: high-frequency generator (1); copper electrode (2); high-frequency torch plasmatron (3); high-frequency torch discharge (4); reactor (5); reactor impeller (6); dispersant (7); unit for water scrubbing of exhaust gases (8); exhaust fan (9); gas analyzer (10); sampling device (11); pyrometer (12); gas duct (13); heater (14)

Plasma unit includes high-frequency generator VChG 8-60/13-01 (oscillatory power up to 60 kW, the operating frequency of 13.56 MHz). High-frequency energy from generator via coaxial output 6 is supplied to the water-cooled copper electrode 2 of high-frequency torch plasmatron 3. Plasmatron generates air plasma jets with temperature to 4000 K. Exhaust fan 9 provides a constant air flow through the plasmatron 3 and reactor 5.

Input unit of plasma gas (air) is provided with an impeller (input area S_{imp} = 25 cm^2). It is placed at the entrance of the plasmatron and is designed for input and swirling the air heat transfer agent into the discharge chamber of the plasmatron. Discharge chamber is made of quartz tube with a diameter of 50 mm and a length of 860 mm.

Reactor impeller 6 is designed for swirling the air heat transfer agent entering the reactor and allows adjusting the input area of the impeller within 0–1650 cm^2.

Gas analyzer 10 and sampling device 11 are made for determining the consist of the exhaust gases after unit for water scrubbing 8 and for measurements with Pitot tube of air heat transfer velocity through plasmatron and the reactor.

Pyrometer 12 is designed for non-contact temperature measurement (through absorption of produced carbon dioxide) of the plasma combustion of inflammable dispersed WOC into reactor.

Experiments on plasma recycling of WPW and MPW were carried out to confirm the calculated results. Wastes recycled in form of model inflammable WOC consisted of WPW and ethanol (instead of poisonous methanol). Ethanol and methanol have close combustion parameters (Table 1).

Table 1. Combustion parameters of MPW components

Name of fuel component	Net calorific value, MJ/kg	Flash-point, °C	Ignition point, °C	Self-ignition point, °C
methanol	19.95	6	13	440
ethanol	26.80	13	18	400

Analysis of combustion parameters of MPW components shows that it need an air jet temperature $T_{jet} \geq 400$ °C for reliable WOC ignition in the reactor.

Figure 5 shows the influence of the anode current of the generator and water content on the operating temperature of the process plasma recycling model dispersed compositions «WPW-ethanol» (flow ≈ 1000 liters per hour).

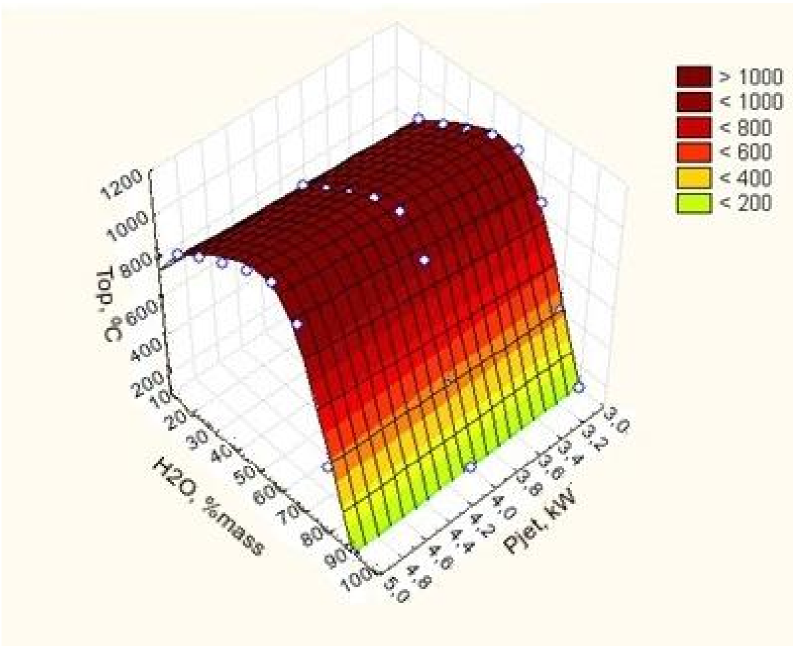

Figure 5. Influence of the anode current of the generator and water content on the operating temperature of the process plasma recycling model compositions «WPW-ethanol»

Analysis of the resulting graphical dependence suggests that the operating temperature in the reactor reaches a maximum temperature T≈1100 ° C at a water content in the composition is ≈40%. The results are consistent with the calculated values. Reject water content in a smaller or larger side reduces the operating temperature of the combustion model of the composition in the reactor.

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5. Conclusion

WPW and MPW plasma recycling in form of optimal WOC can significantly reduce the specific energy consumption for the process as well as to apply magnetic separation for efficient extraction of iron-containing pigments being plasma recycling products. All the obtained calculated and experimental results may be used for creating of industrial equipment for plasma obtaining of iron-containing pigments from WPW and MPW.

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