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Comparative analysis of polychlorinated biphenyl decomposition processes in air or argon (+ oxygen) thermal plasma

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Abstract

Thermal plasmas may solve one of the biggest toxic waste disposal problems. The disposal of polychlorinated biphenyls (PCBs) is a long standing problem which will get worse in the coming years, when 180 000 tons of PCB-containing wastes are expected to accumulate in Europe (Hot ions break down toxic chemicals, *New Scientist*, 16 April 1987, p. 24.). The combustion of PCBs in ordinary incinerators (at temperature $T \sim 1100$ K, as measured near the inner wall of the combustion chamber (European Parliament and Council Directive on Incineration of Waste (COM/99/330), *Europe energy*, 543, Sept. 17, 1999, 1–23.)) can cause more problems than it solves, because highly toxic dioxins and dibenzofurans are formed if the combustion temperature is too low ($T < 1400$ K). The paper presents a thermodynamic consideration and comparative analysis of PCB decomposition processes in air or argon (+ oxygen) thermal plasmas. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polychlorinated biphenyls; Air; Argon

1. Introduction

In the future, the disposal of toxic and hazardous waste materials must be replaced by destruction or decomposition in order to reduce environmental pollution risk caused by other means of disposal. The conventional method for such destruction is combustion in incinerators. But some substances (like transformer oils) containing polychlorinated

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biphenyl isomers (PCBs) with the general formula $C_{12}H_{10-n}Cl_n$ require a relatively high temperature for complete decomposition. For incineration of halogenated organic substances, the temperature level of the gas products after combustion (last injection of air) should be above 1400 K (even at the chamber wall) for at least 2 s [1]. Such conditions should guarantee a high destruction level in modern high temperature incinerators. As an alternative method, plasma arc processing is well suited for destruction of liquid materials containing PCBs [2,3] or equipment contaminated with PCBs [4] due to its capability of realizing any desired high temperature level ($2000\text{ K} < T < 10,000\text{ K}$) independently of chemical composition. A plasma process usually involves two steps. The high temperature level of the plasma guarantees atomization of various dangerous and complex molecules in a first step, which is followed by chemical or thermal quenching that enables formation of desired products like simple components (hydrogen, carbon monoxide, carbon dioxide, hydrogenchloride gas) or compounds that might even have a market value.

This paper presents thermodynamic considerations of two different plasma decomposition processes for transformer oils containing PCBs, illustrating wide possibilities of plasma processes for effective destruction of gas or liquid toxic materials.

2. Computation method

The thermodynamic method, used¹ for chemical equilibrium composition and system enthalpy computation, is based on the Mass Action Law [5]. This method is highly efficient, especially for a low-temperature thermal plasma ($T < 6000\text{ K}$) if the pressure level is about 1 bar. A thermal plasma at these conditions follows ideal gas behavior because: (i) the temperature is sufficiently high (1000 K to 6000 K) at relatively low pressure, and (ii) ion (and electron) concentrations in these conditions generally are very small.

The first step in the thermodynamic modeling of the chemical equilibria is a decision about the number of gas and condensed (solid or liquid) phase species to be considered. Let this number be m , the number of dense (solid and liquid) phase species be f and the number of atomic species be q , then $m - q$ mass action equations will determine equilibrium composition. In other words, $m - q$ equilibrium constants pertain. The equilibrium constants are usually specified for the decomposition reactions to the constituent atoms; then all the equations are independent, such that

$$K_j(T) = \prod_{i=1}^q \frac{p_i^{a_{ij}}}{p_j} \quad (j = 1, 2, \dots, m - q) \quad (1)$$

where p_i is the partial pressure of the atomic species, p_j is the partial pressure of the molecular species, a_{ij} is the stoichiometric coefficient of decomposition reactions, and $K_j(T)$ is the mass action constant for decomposition reactions j into the atoms.

¹ An alternative approach is based on the free enthalpy (Gibbs energy) minimization [6].

In the case of condensed (solid or liquid) substances that do not form solid solutions, the application of mass action law (based on the constant saturation pressure p_l^c above the condensed phase at a fixed temperature T , f), other equations occur. These are of the form

$$K_l^c(T) = p_l^c \quad (l = 1, 2, \dots, f) \tag{2}$$

where subscript l indicates either atomic or molecular chemical species.

For an ideal gas mixture, Dalton’s law is introduced in the form

$$\sum_{l=1}^g p_l = p \tag{3}$$

where g is the number of gas species and p is the total pressure of the mixture.

In order to close the system of equations, the $q - 1$ mass balance equations are included

$$\frac{\sum_{l=1}^g a_{ol} p_l + \sum_{l=1}^f a_{ol} p v_l^c}{\sum_{l=1}^g a_{dl} p_l + \sum_{l=1}^f a_{dl} p v_l^c} = \frac{O}{D} \tag{4}$$

where a_{ol} and a_{dl} are the numbers of o and d atomic species comprising the product molecule l ; v_l^c is the ratio of number of moles of condensed phase of constituent l to total number of moles in gas phase; O and D are the o and d atomic species content in the reactants, respectively.

The total enthalpy of the system, H_s , at temperature T , is calculated by adding an enthalpy of constituents (gaseous and condensed)

$$H_s(T) = n_g \left[\sum_{l=1}^g v_l H_l(T) + \sum_{l=1}^f v_l^c H_l^c(T) \right] \tag{5}$$

where n_g is the total number of moles in gaseous phase, v_l is the mole fraction of gas constituent l (ratio of number of moles of gas constituent l to total number of moles in gas phase), H_l [kJ/mol] and H_l^c [kJ/mol] are mole enthalpies of constituent l in gas and condensed phase, respectively, defined by the relationship

$$H_l(T) = -T^2 \left[\frac{\partial(G_l/T)}{\partial T} \right]_{p, v_l} = T^2 \left[\frac{\partial\Phi_l}{\partial T} \right]_{p, v_l} + \Delta_f H_l(T=0) \tag{6}$$

where $\Delta_f H_l(0)$ is the heat of formation of constituent l , from elements at standard state, for temperature $T = 0$ K, and Φ_l is the modified free enthalpy of constituent l defined as [5]

$$\Phi_l(T) = \frac{G_l(T) - H_l(T=0)}{T} = S_l(T) - \frac{H_l(T) - H_l(T=0)}{T} \tag{7}$$

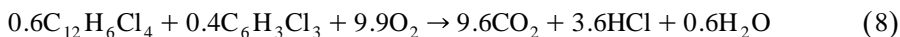
where G is the Gibbs energy and S the entropy. For more details about the computation method see Ref. [5].

The polynomial coefficients of the temperature dependence of modified free enthalpies, chemical reaction enthalpy change, and the heat of formation (from elements at standard state and temperature 0 K) of constituents in the system, are taken from Ref. [7], which are equivalent to those in JANAF [8] but more complete and more convenient to use.

3. Preliminary considerations

Typical transformer oil on PCBs bases, Askarel, contains about 65% of tetrachlorobiphenyl and 35% of trichlorobenzene (for external usage at temperature $T > -40^{\circ}\text{C}$). For internal use (for $T > -25^{\circ}\text{C}$), transformer oil, containing for example 75% of tetrachlorobiphenyl and 25% of trichlorobenzene, is used. The density of Askarel is about 1.5 kg/l.

For considerations in this paper, a transformer oil with generic formula $(\text{C}_{12}\text{H}_6\text{Cl}_4)_{0.6}(\text{C}_6\text{H}_3\text{Cl}_3)_{0.4}$ (and typical molecular mass of 247.7544 g/mol) corresponding to 70.7% of tetrachlorobiphenyl and 29.3% of trichlorobenzene is used. Enthalpy (including heat of formation) of this transformer oil at $T = 298.15\text{ K}$ (25°C) is calculated from the heat of combustion of transformer oils on PCB bases (which may have values from 3300 kJ/mol to 5100 kJ/mol), using the chemical formula



and heat balance

$$(H + \Delta H_f)_{\text{Trs.oil}} + 9.9H_{\text{O}_2} = 9.6(H_{\text{CO}_2} + \Delta H_{f,\text{CO}_2}) + 3.6(H_{\text{HCl}} + \Delta H_{f,\text{HCl}}) + 0.6(H_{\text{H}_2\text{O}} + \Delta H_{f,\text{H}_2\text{O}}) + \Delta H_{\text{comb}}$$

For minimal ($\Delta H_{\text{comb}} = 3300\text{ kJ/mol}$) and medium ($\Delta H_{\text{comb}} = 4200\text{ kJ/mol}$) values of heat of combustion of transformer oil, calculated values for $(H + \Delta H_f)_{\text{Trs.oil}}$ are: -934.28 kJ/mol and -34.28 kJ/mol , respectively.

4. Results and discussions

4.1. Decomposition in air thermal plasma

The computation of the equilibrium composition and enthalpy of PCB transformer oil–air system (for oxygen excess of 10% with respect to chemical Eq. (8), i.e. for the coefficient of air excess $\alpha = 1.1$), was conducted for 88 possible chemical species (see Table 1), at atmospheric pressure and for the temperature range between 1000 and 6000 K.

The temperature dependence of equilibrium composition for PCB oil–air plasma system (for $\alpha = 1.1$) with atomic ratio C:H:Cl:O:N:Ar = 0.0793:0.0396:0.0297:0.1799:0.6675:0.004, is given in Fig. 1. All species are in the gaseous state. A small mole fraction of NO^+ ions and electrons exist at higher temperatures only (about 0.01% at $T = 6000\text{ K}$).

Table 1

Considered chemical species as possible PCBs oil decomposition products

Except for the gaseous chemical species, condensed C(s)– graphite was also considered as a possible solid product

C	H	Cl	O	N	HCl	CH	CN	Ar	e ⁻	H ⁻
C ₂	H ₂	Cl ₂	O ₂	N ₂	HCN	CH ₂	CNN	Cl ⁻	CN ⁻	C(s)
C ₃	H ₂ O	ClO	CO	NO	HNC	C ₂ H	CCN	CHCl	CHCl ₂	NO ₂ ⁻
CCl	NH	ClO ₂	CO ₂	NO ₂	HNO	CH ₃	CNC	NH ₂ OH	CHCl ₃	CH ₂ Cl ₂
CCl ₂	NH ₃	Cl ₂ O	C ₂ O	N ₂ O	HNO ₂	CH ₄	NCN	C ₂ H ₃ Cl	C ₂ H ₂ Cl ₂	C ₂ HCl
C ₂ Cl	HCO	CICO	NCO	N ₂ O ₃	HNO ₃	C ₂ H ₂	C ₂ N ₂	C ₂ HCl ₃	C ₂ H ₂ Cl ₂	1–1–C ₂ H ₂ Cl ₂
CCl ₃	C ₂ Cl ₂	Cl ₂ CO	ClNO	N ₂ O ₄	HCCN	C ₂ Cl ₅	C ₂ Cl ₆	CH ₂ Cl	NO ⁺	<i>trans</i> -C ₂ H ₂ Cl ₂
CCl ₄	C ₂ Cl ₃	C ₂ Cl ₄	ClNO ₂	N ₂ O ₅	HOCl	NO ₃ ⁻	–	NH ₂ NO ₂	CN ⁺	<i>cis</i> -C ₂ H ₂ Cl ₂

If the equilibrium mixture of PCB–oil and air plasma is at about $T = 3000$ K, concentration of all harmful and toxic gases except CO, HCl, Cl, Cl₂, ClO and NO is less (frequently a few order of magnitude below, including such substances as phosgene Cl₂CO, cyanics CN, HCN) than prescribed allowable values (see Fig. 1 and Appendix A).

The considerable quantity of HCl, Cl, Cl₂, NO (and small but not allowed quantity of ClO) in the flue gases needs a section for absorption (scrubbing) of these gases in a plasma plant for the PCB–oil decomposition.

The significant quantity of CO and H₂ in the flue gases (see Fig. 1a) enables its use (after scrubbing) as an energetic gas in situ. If use of CO and H₂ in situ is not possible, they (and hydrocarbon components, CH, CH₂, C₂H) must be burned before emitting flue gases to the atmosphere.

The temperature dependence of total enthalpy (including heat of formation and latent heat of phase transformation), per 1 mol*, for the system in Fig. 1 is presented in Fig. 2 (curve no. 2) together with the dependence for pure air (curve no. 1). One mol* (signed with asterisk) is defined as the quantity of the system, which consists of 1 mole of atoms (of all elements in the systems) in total. For example, 1 mol* of the system in Fig. 1 consists of 0.0793 mol of C atoms plus 0.0396 mol of H atoms plus 0.0297 mol of Cl atoms plus 0.1799 mol of O atoms plus 0.6675 mol of N atoms plus 0.004 mol of Ar atoms. One mol* of air plasma consists of 0.78387 mol of N atoms + 0.21126 mol of O atoms + 0.00015 mol of C atoms + 0.00472 mol of Ar atoms. Conditional molecular mass (per mol*) of air plasma is 14.5526 g/mol*.

4.1.1. Determination of energy consumption

For temperature $T_1 = 5200$ K, the enthalpy of air plasma is $H_{1,air} = 158.1$ kJ/mol* (see Fig. 2, curve no. 1). The enthalpy of air at $T = 298.15$ K (calculated from enthalpies [7] for N₂, O₂, CO₂, Ar) is $H_{0,air} = 8.53$ kJ/mol. Conditional molecular mass of the air plasma is 14.5526 g/mol* (see Section 3). Mean molecular mass of air is 28.9727 g/mol (quantity of 1 mol* of air is equivalent to $14.5526/28.9727 = 0.5023$ mol of air).

It is presumed that heat losses to surroundings, Q , are 40% of air plasma enthalpy difference $H_{1,air} - 0.5023 \times H_{0,air}$, i.e. $Q = 0.4 \times (158.1 - 0.5023 \times 8.53) = 61.53$ kJ/mol*.

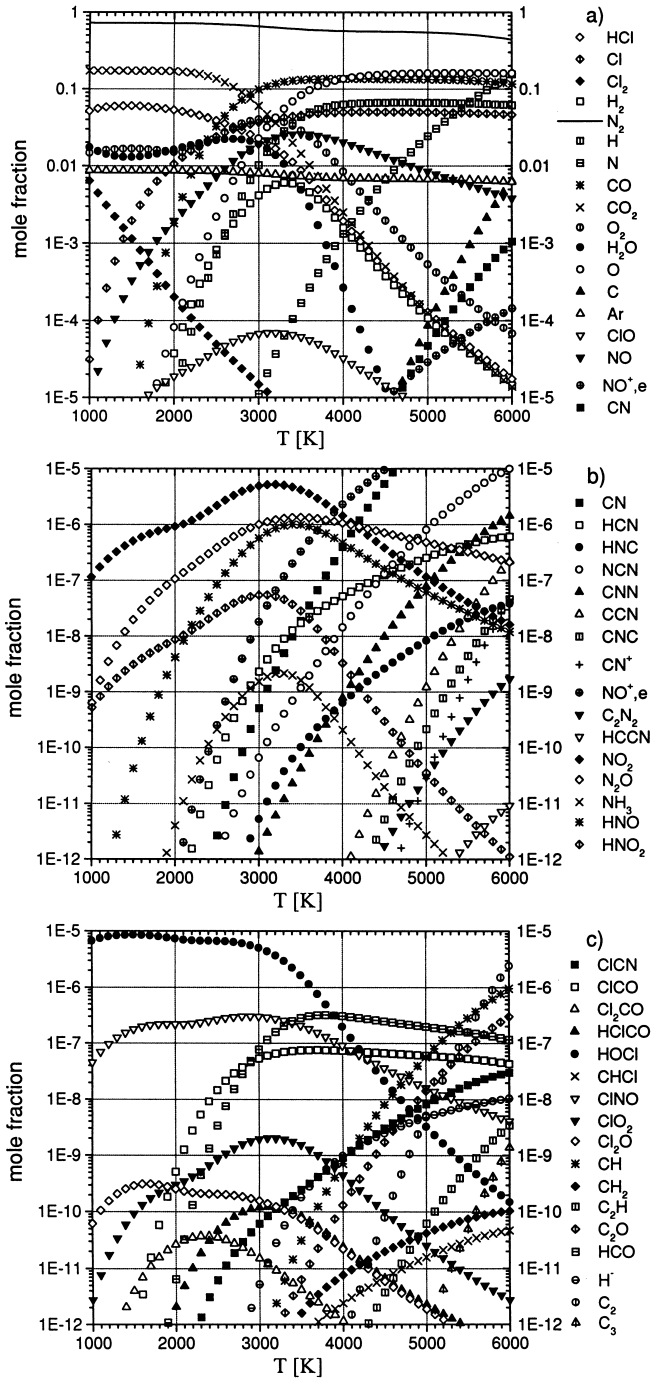


Fig. 1. Equilibrium composition of the PCBs oil–air thermal plasma system for $\alpha = 1.1$ (C:H:Cl:O:N:Ar = 0.0793:0.0396:0.0297:0.1799:0.6675:0.004). (a) Main constituents; (b, c) other species (minor constituents).

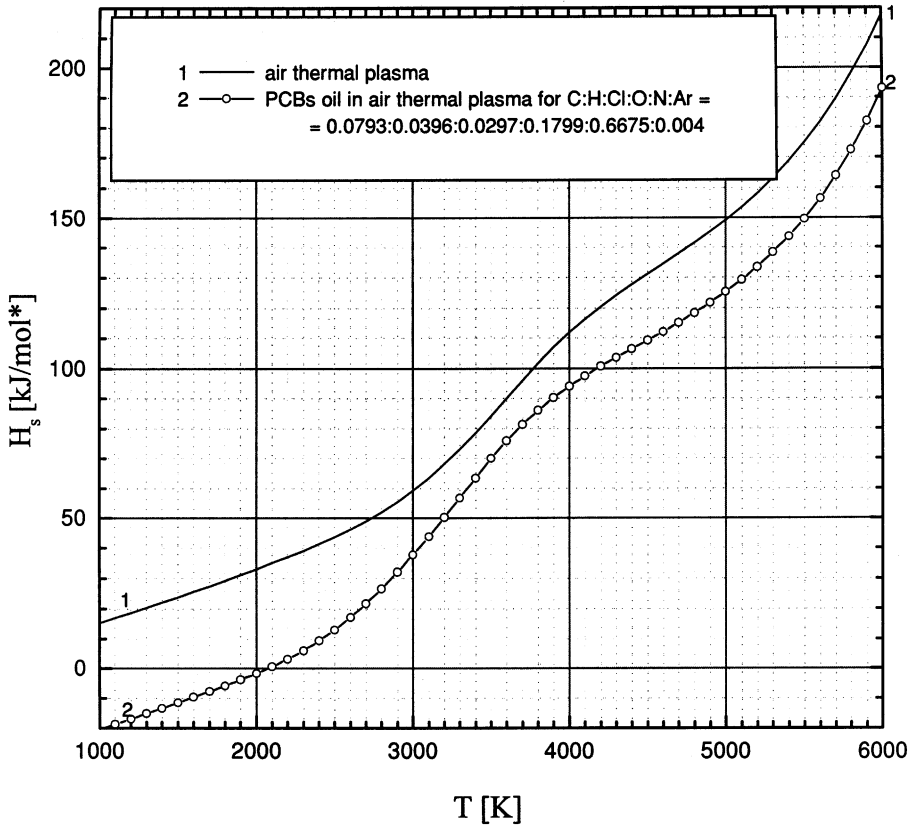


Fig. 2. Temperature dependence of enthalpy for air plasma and PCBs oil–air system.

The system from Fig. 1 can be obtained by injection of 0.00825 mol of transformer oil with the conditional formula $(C_{12}H_6Cl_4)_{0.6}(C_6H_3Cl_3)_{0.4}$, to 0.85158 mol* of air plasma. For energy savings, 40% of air mass is introduced to the system as secondary cold air (at $T = 298.15$ K), and 60% as air plasma. The enthalpy of such a system will be

$$\begin{aligned}
 H_s &= 0.6 \times 0.85158 \times H_{1,air} + 0.00825 \times (H + \Delta H_f)_{Trs.oil} \\
 &\quad + 0.4 \times 0.85158 \times 0.5023 \times H_{0,air} - 0.6 \times 0.85158 \times Q \\
 &= 0.6 \times 0.85158 \times 158.1 + 0.00825 \times (-934.28) \\
 &\quad + 0.4 \times 0.4277 \times 8.53 - 0.6 \times 0.85158 \times 61.53 \\
 &= 42.26 \text{ kJ/mol}^*
 \end{aligned}$$

or

$$\begin{aligned} H_s &= 0.6 \times 0.85158 \times 158.1 + 0.00825 \times (-34.28) \\ &\quad + 0.4 \times 0.4277 \times 8.53 - 0.6 \times 0.85158 \times 61.53 \\ &= 49.69 \text{ kJ/mol}^* \end{aligned}$$

for two different values of transformer (PCBs) oil enthalpy (at $T = 298.15 \text{ K}$) given in Section 3.

Temperature of the system corresponding to two calculated values of enthalpy H_s determined from Fig. 2 (curve no. 2) is $T_s \approx 3050 \text{ K}$ or $T_s \approx 3200 \text{ K}$.

Transformer (PCBs) oil (1 l) with the generic formula $(\text{C}_{12}\text{H}_6\text{Cl}_4)_{0.6}(\text{C}_6\text{H}_3\text{Cl}_3)_{0.4}$, conditional molecular mass of 247.7544 g/mol and density of 1500 g/l, consists of $1 \times 1500/247.7544 = 6.054 \text{ mol/l}$. The decomposition of 1 l of this transformer oil needs $0.6 \times 0.85158 \times 6.054/0.00825 = 374.95 \text{ mol}^*$ of air plasma. The energy consumption for considered process of transformer (PCBs) oil decomposition will be

$$\begin{aligned} 374.95 \times (H_{1,\text{air}} - 0.5023 \times H_{0,\text{air}}) &= 374.5 \times (158.1 - 0.5023 \times 8.53) \\ &= 57673 \text{ kJ/l} = 16.02 \text{ kWh/l} \end{aligned}$$

4.2. Decomposition in argon (+ oxygen) thermal plasma

The computation of the equilibrium composition and enthalpy of PCB transformer oil–argon–oxygen system at atmospheric pressure was conducted for the temperature range between 1000 and 6000 K with the chemical species given in Table 1, except the species that includes the N atom (as possible products of decomposition).

The temperature dependence of equilibrium composition for the system PCB oil–argon–oxygen plasma, with atomic ratio² C:H:Cl:O:Ar = 0.2:0.1:0.075:0.4125:0.2125, is given in Fig. 3. All species are in the gaseous state. A small mole fraction of C^+ ions and electrons exist at higher temperatures only (about 0.02% at a temperature $T = 6000 \text{ K}$).

At temperature $T = 3000 \text{ K}$, the concentration of all harmful and toxic gases except CO, HCl, Cl, Cl_2 , ClO, is below (frequently a few order of magnitude below, including such as phosgene– Cl_2CO) the prescribed allowable values (see Fig. 3 and Appendix A). As in the case of PCBs oil decomposition in air thermal plasma, the considerable quantity of HCl, Cl, Cl_2 (and small but not allowed quantity of ClO) present in flue gases, needs a section for absorption (scrubbing) after plasma reactor. Compared with air thermal decomposition process, in the argon + oxygen process there is no nitrogen oxides or cyanics (CN, HCN) in the flue gasses. The significant quantity CO and H_2 (and hydrocarbon ingredients, CH, CH_2 , C_2H) can be burned at the exit of the plant.

The temperature dependence of total enthalpy (per 1 mol^{*}) for the system from Fig. 3 is presented in Fig. 4, and total enthalpy for argon plasma is given in Table 2.

² This system corresponds (approximately) to experimentally investigated PLASCON™ process [3] of PCBs waste plasma destruction.

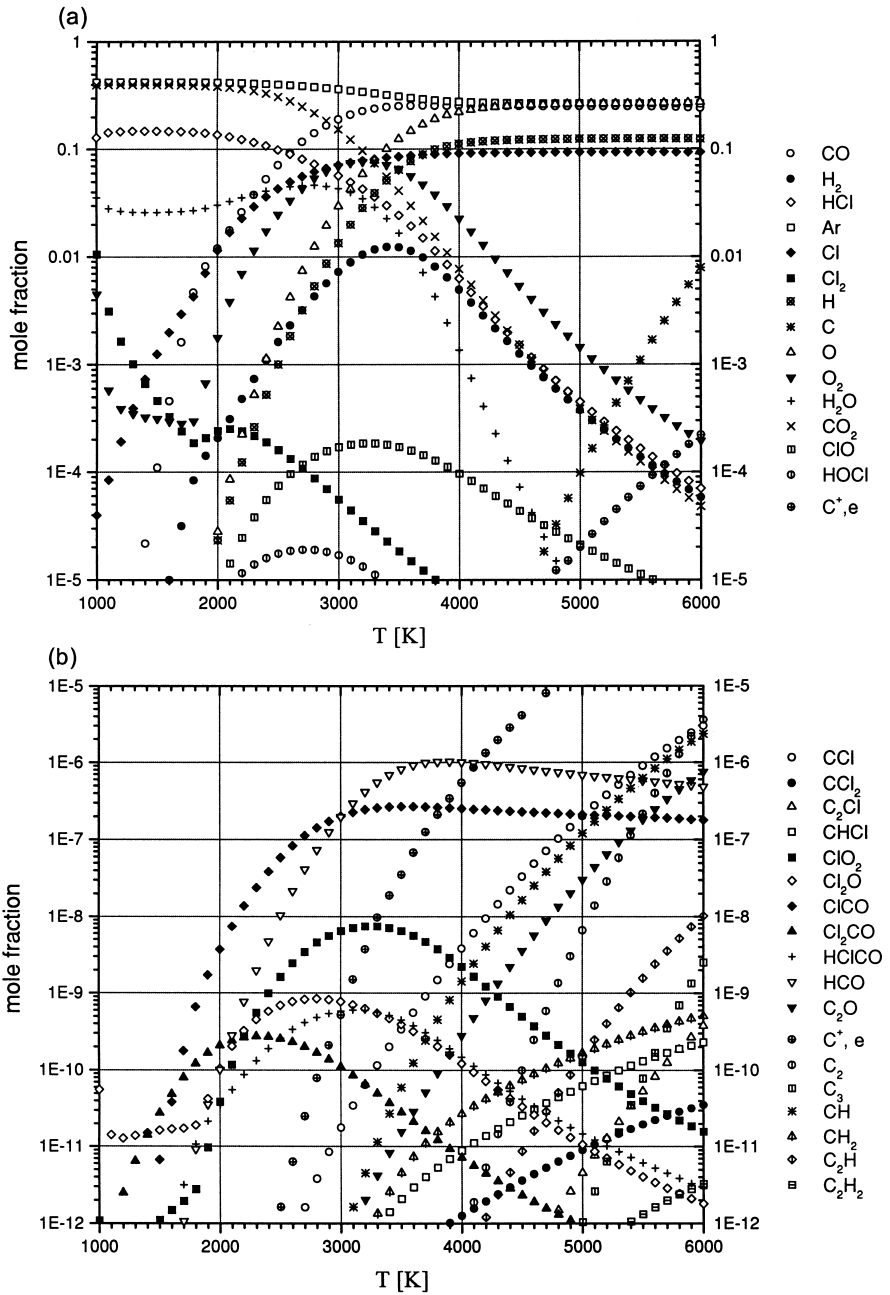


Fig. 3. Equilibrium composition of the PCBs oil-argon-oxygen thermal plasma system (C:H:Cl:O:Ar = 0.2:0.10:0.075:0.4125:0.2125). (a) Main constituents; (b) other species (minor constituents).

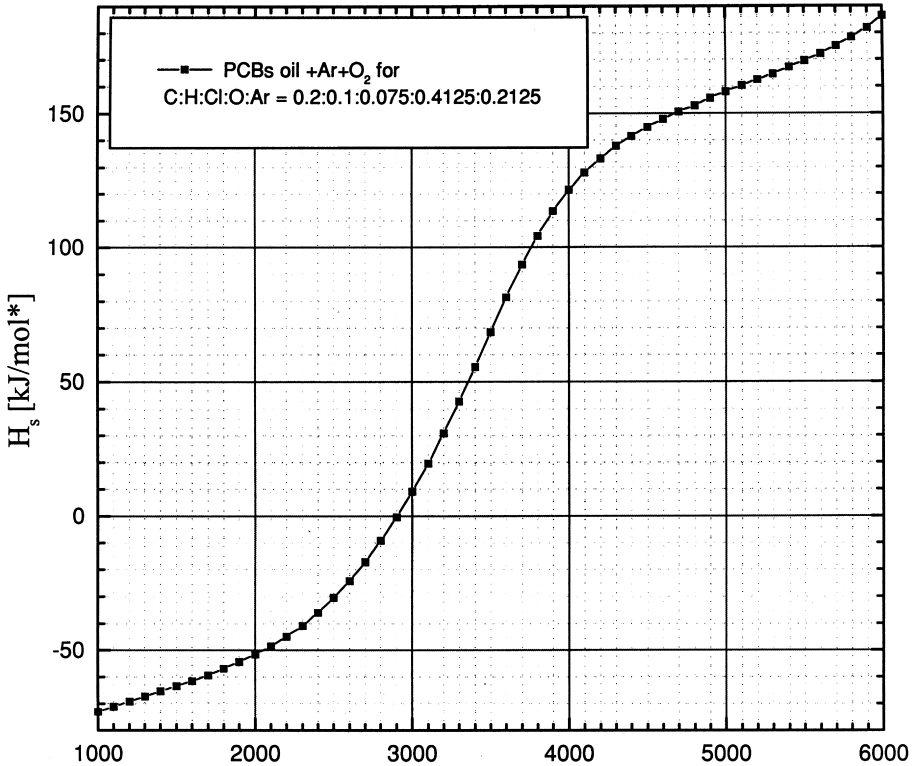


Fig. 4. Temperature dependence of enthalpy for PCBs oil–argon–oxygen system.

4.2.1. Determination of energy consumption

For temperature $T_1 = 10,000$ K, the enthalpy of argon plasma is $H_{1,Ar} = 243.5$ kJ/mol* (see Table 2). The enthalpy of argon at $T = 298.15$ K is [7] $H_{0,Ar} = 6.197$ kJ/mol and enthalpy of oxygen at $T = 298.15$ K is [7] $H_{0,O_2} = 8.68$ kJ/mol.

It is presumed that heat losses to surroundings, Q , are 40% of the argon plasma enthalpy difference $H_{1,Ar} - H_{0,Ar}$: $Q = 0.4 \times (243.5 - 6.197) = 94.92$ kJ/mol*.

The system from Fig. 3 can be obtained by injection of 0.02083 mol of transformer oil with generic formula $(C_{12}H_6Cl_4)_{0.6}(C_6H_3Cl_3)_{0.4}$, and 0.20625 mol of oxygen (O_2) to 0.2125 mol* of argon plasma. The enthalpy of such a system will be

$$\begin{aligned}
 H_s &= 0.2125 \times H_{1,Ar} + 0.02083 \times (H + \Delta H_f)_{Trs.oil} \\
 &\quad + 0.20625 \times 0.4277 \times H_{0,O_2} - Q \\
 &= 0.2125 \times 243.5 + 0.02083 \times (-934.28) \\
 &\quad + 0.20625 \times 8.68 - 0.2125 \times 94.92 \\
 &= 13.99 \text{ kJ/mol}^*
 \end{aligned}$$

Table 2
Enthalpy of argon plasma

<i>T</i> [K]	<i>H</i> [kJ/mol*]	<i>T</i> [K]	<i>H</i> [kJ/mol*]	<i>T</i> [K]	<i>H</i> [kJ/mol*]	<i>T</i> [K]	<i>H</i> [kJ/mol*]	<i>T</i> [K]	<i>H</i> [kJ/mol*]
1100	22.86	3900	81.07	6700	139.5	9500	218	12300	516.5
1200	24.94	4000	83.14	6800	141.6	9600	222.5	12400	537.4
1300	27.02	4100	85.22	6900	143.8	9700	227.4	12500	559.4
1400	29.1	4200	87.3	7000	145.9	9800	232.4	12600	582.3
1500	31.18	4300	89.38	7100	148.1	9900	237.8	12700	606.3
1600	33.26	4400	91.46	7200	150.3	10000	243.5	12800	631.3
1700	35.34	4500	93.54	7300	152.5	10100	249.5	12900	657.3
1800	37.41	4600	95.62	7400	154.8	10200	255.8	13000	684.4
1900	39.49	4700	97.7	7500	157	10300	262.5	13100	712.6
2000	41.57	4800	99.77	7600	159.3	10400	269.7	13200	741.8
2100	43.65	4900	101.9	7700	161.7	10500	277.2	13300	772
2200	45.73	5000	103.9	7800	164	10600	285.2	13400	803.2
2300	47.81	5100	106	7900	166.5	10700	293.6	13500	835.4
2400	49.89	5200	108.1	8000	168.9	10800	302.6	13600	868.5
2500	51.97	5300	110.2	8100	171.5	10900	312	13700	902.5
2600	54.04	5400	112.3	8200	174.1	11000	322	13800	937.4
2700	56.12	5500	114.3	8300	176.7	11100	332.6	13900	973
2800	58.2	5600	116.4	8400	179.5	11200	343.9	14000	1009
2900	60.28	5700	118.5	8500	182.3	11300	355.7	14100	1046
3000	62.36	5800	120.6	8600	185.3	11400	368.3	14200	1084
3100	64.44	5900	122.7	8700	188.3	11500	381.5	14300	1122
3200	66.52	6000	124.8	8800	191.5	11600	395.5	14400	1160
3300	68.59	6100	126.8	8900	194.8	11700	410.2	14500	1199
3400	70.67	6200	128.9	9000	198.2	11800	425.8	14600	1238
3500	72.75	6300	131	9100	201.8	11900	442.1	14700	1276
3600	74.83	6400	133.1	9200	205.6	12000	459.4	14800	1315
3700	76.91	6500	135.3	9300	209.5	12100	477.5	14900	1354
3800	78.99	6600	137.4	9400	213.6	12200	496.5	15000	1392

or

$$\begin{aligned}
 H_s &= 0.2125 \times 243.5 + 0.02083 \times (-34.28) \\
 &+ 0.20625 \times 8.68 - 0.2125 \times 94.92 \\
 &= 32.74 \text{ kJ/mol}^*
 \end{aligned}$$

for the two values of transformer (PCBs) oil enthalpy (at $T = 298.15 \text{ K}$) given in Section 3.

Temperature of the system corresponding to calculated values of enthalpy H_s could be determined from Fig. 4

$$T_s \approx 3050\text{K or } T_s \approx 3200\text{K}$$

Transformer (PCBs) oil (1 l) with the conditional formula $(C_{12}H_6Cl_4)_{0.6}(C_6H_3Cl_3)_{0.4}$, conditional molecular mass of 247.7544 g/mol and density of 1500 g/l, consists of $1 \times 1500/247.7544 = 6.054 \text{ mol/l}$. For the decomposition of 1 l of this transformer oil,

one needs $0.2125 \times 6.054 / 0.02083 = 61.76 \text{ mol}^*$ of argon plasma. The energy consumption of the considered process of transformer (PCBs) oil decomposition will be

$$\begin{aligned} 61.76 \times (H_{1,\text{Ar}} - H_{0,\text{Ar}}) &= 61.76 \times (243.5 - 6.197) \\ &= 14655.8 \text{ kJ/l} = 4.07 \text{ kW h/l} \end{aligned}$$

This value is in good agreement with the value of 4.11 kW h/l calculated from experimental data reported in literature [3].

5. Comparative analysis

Presented results of the calculations show that the process of PCBs oil decomposition in air thermal process needs almost four times greater energy consumption (per unit quantity) than the decomposition process in argon(+ oxygen) thermal plasma. It means that four times greater power and therefore capital costs are needed for the process of PCBs oil decomposition in air thermal plasma. However, for complete economic analysis, it is necessary to take into consideration a significant consumption of argon and oxygen in argon(+ oxygen) thermal plasma process of PCBs oil decomposition, while the process in air plasma needs compressed air only. (Both considered processes need other precursors as, for example, 5% NaOH water solution for scrubbing product gasses).

Process of PCBs oil destruction in argon(+ oxygen) thermal plasma needs (see Section 4.2):

$$\begin{aligned} 61.76 \text{ mol of argon per 1 l of PCBs (transformer) oil, i.e. } 61.76 \times M_{\text{Ar}} &= 61.76 \times 39.95 = 2467 \text{ g/l; specific consumption of argon is 2.467 kg/l.} \\ 61.76 \times 0.20625 / 0.2125 \times M_{\text{O}_2} &= 59.94 \times 32 = 1918 \text{ g/l, that is 1.918 kg/l of oxygen.} \end{aligned}$$

Process of PCBs oil destruction in air thermal plasma needs (see Section 4.1):

$$(374.5 \times 14.5526 / 28.9727 + 0.4 \times 0.4277 \times 6.054 / 0.00826) \times M_{\text{Air}} = 313.5 \times 28.9727 = 9083 \text{ g/l of compressed air (Specific consumption of air is 9.083 kg/l).}$$

With respect to environmental impact, the PCB oil decomposition in argon(+ oxygen) thermal plasma decomposition process has some advantages because in this case, nitrogen oxides or cyanics (CN, HCN) cannot be present in flue gasses.

6. Conclusions

Using a thermodynamic method of chemical composition and total enthalpy computation, comparative analysis of two PCBs (transformer) oil decomposition processes was conducted. Analyzed processes are:

- PCB oil decomposition in air thermal plasma, and
- PCB oil decomposition in argon(+ oxygen) thermal plasma.

Based on presented results one can conclude:

1. Energy consumption and therefore the necessary plant power, i.e. capital costs per unit quantity of decomposed PCBs oil in the air thermal plasma process, is almost four times greater than in the argon(+ oxygen) thermal plasma process.
2. Costs for gasses used in the process (air, argon and oxygen) are greater in case of argon(+ oxygen) thermal plasma process.
3. Complete economic analysis of two presented processes is needed to make a conclusion, which of the two considered processes is preferred. Generally, with respect to operating costs, if the cost of argon and oxygen is high, the air thermal plasma process may have an advantage for decomposition of large quantities of PCBs (transformer) oils, and the argon(+ oxygen) thermal plasma process is more suitable for decomposition of smaller quantities of PCBs (transformer) oils.
4. Ecologically, the argon(+ oxygen) thermal plasma process may have a certain advantage because in this process there are no nitrogen atoms and therefore nitrogen oxide or cyanics (CN, HCN) cannot be present in flue gasses.

Destruction efficiency of both thermal plasma decomposition processes is very high as was experimentally shown by other authors:

For PCB waste decomposition in air thermal plasma [2], experimental value of destruction efficiency is 99.999999% while the EPA Requirement is 99.99999%. Results from two independent laboratories showed destruction efficiency of 99.999999% for PCB and of 99.999995% for trichlorobenzen, as reported for PCBs waste decomposition in argon(+ oxygen) thermal plasma process [3].

Appendix A. Allowed concentrations for new plants (From European Environmental Legislation [1,9])

	mg/m ³		mg/m ³
Particulates	5	Chlorine (Cl ₂)	5
Carbon monoxide (CO)	50	Hydrogenchloride (HCl)	10
Nitrogen oxides (expressed as NO ₂)	200	Methylchloride (CH ₃ Cl)	20
Ammonia (NH ₃)	30	Tetrachloromethane (CCl ₄)	20
Organic species (expressed as C)	10	Cyanogen chloride (CNCl)	1
Dioxins and dibenzofurans (asTEQ)	0.0000001	Phosgene (COCl ₂)	1

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