ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 4, pp. 801–807. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.V. Artemov, V.A. Bul'ba, S.A. Voshchinin, Yu.A. Krutyakov, A.A. Kudrinskii, I.I. Ostryi, A.V. Pereslavtsev, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 6, pp. 19–25.

Products of High-Temperature Plasma Conversion of Solid Production and Consumption Wastes. Comparative Quality Assessment of Plasma Conversion and Incineration Products

A. V. Artemov, V. A. Bul'ba, S. A. Voshchinin, Yu. A. Krutyakov,
A. A. Kudrinskii, I. I. Ostryi, and A. V. Pereslavtsev

KORTEZ OOO, ul. Kuusinena 21A, Moscow, 125252 Russia
e-mail artemov.a@kortez.org

Received December 15, 2010

Abstract—The plasma technology provides the possibility to prevent hazardous industrial waste formation. Moreover, it is reasonable to include into the pyrogas treatment technology the catalytic stages of steam and carbon dioxide reforming and Fischer−Tropsch hydrocarbon synthesis. Plasma technology allows waste to serve as an inexhaustible source of raw materials for production of electricity, hydrogen, and fuels.

DOI: 10.1134/S1070363212040354

The commonly accepted technology of incineration of production and consumption wastes makes use of combustion of natural gas (or other combustible gases) in fluidized bed apparatuses at temperatures of up to 850°C. Incineration provides an efficient way to decrease the volume of wastes subject to landfill disposal, with simultaneous production of energy (heat or electric). According to [1], the volume of wastes after combustion at incineration plants is decreased by 80−85%. At the same time, the incineration process poses environmental threat. Emissions of incineration plants contain toxic substances, specifically polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) [2], polycyclic hydrocarbons [3], heavy metals [4], as well as health-hazardous aerosols [5].

Much effort is being directed toward reduction of hazardous emissions from incineration plants, primarily toward improvement of gas purification systems including a great number of scrubbers, sleeve filters, absorbers, electrostatic filters, and other aggregates. Sleeve and electrostatic filters especially effectively trap coarse particular matter in emission gases. At the same time, fine particles (aerodynamic diameter less than 2.5 μm) which are the most dangerous for human and animal health are virtually not trapped in the most part of commonly applied gas purification systems. Note that the ability to trap submicron particles is not at all regulated in technological and operational documentation for dust collection systems, as well as in environmental safety certificates for such systems. Scarce evidence is only available showing that the minimum size of particles trapped by electrostatic and fiber filters spans the range 0.1−1 μm [5, 7].

It is traditionally considered that the greatest hazard to the environment is associated with solid residues (ash) of solid waste incineration. Ash contains 3−7% of the so-called fly ash, as well as much heavy metals (Cd, Pb, Cu, Cr, and others) as oxides, carbonates, chlorides, and other salts [8, 9] (Table 1). The chemical state of metals in incinerated wastes favors their subsequent fairly easy and permanent release to the environment in the places of their final disposal (soils, ground waters, etc.) or secondary use.

However, the environmental hazard of aerosols formed upon waste incineration and passing through gas purification systems is not infrequently underestimated. Submicron particle aerosol emissions have quite a strong health impact [10, 11]. Together with emission gases they enter the atmosphere. On respiration submicron particles enter directly to lungs. Moreover, they possess enhanced penetrability and are able to pass cellular membranes and affect vitally

Table 1. Results of elemental analysis of solid waste incineration ash at incineration plants (according to [9])

Element/ ion	Content of element (mg kg^{-1}) or ion (mg l^{-1})		
	cyclone ash	scrubber ash	reactor ash
Lead	650±14.8	1229±84.1	1230±33.2
Cadmium	53±1.7	130±5.9	93±0.6
Chromium	274±24.6	26±1.7	248±12.4
Copper	850±89.1	740±13.8	1130±47.9
Zinc	5540±163.0	7780±256.0	8210±184.0
Nitrite	542.6±3.7	1563.7±23.9	1041.3±4.9
Nitrate	1168.1±26.1	24.5±1.0	210.5±2.6
Chloride	222.7±6.4	21050±62.9	32000±1000

important organelles (inducing carcinogenesis and mutagenesis) [12].

In many developed counties atmospheric emissions of submicron particles are regulated at the legal level. However, these standards relate to the total mass of aerosol emissions, the most part of which falls on coarse particles effectively trapped in sleeve and electrostatic filters. Most modern standards regulating emissions of fine particles are based on the PM$_x$ value defined as the concentration of the smallest particles: either 10 μm or, like in the USA, 2.5 μm (US EPA, 2006). Usually, the rate of one or another disease, estimated by the results of medical examinations, is correlated exclusively with the gross particle emission. As applied to emissions of incineration plants, such parameters are not fully correct. In this case, no attention is paid to the fact that aerosols present in emissions of incineration plants contain PCDD, PCDF, and other toxicants, as well as much adsorbed heavy metals (Pb, Cd, Cr, Fe, Ni, Cu, etc.) [13, 14].

The problem of formation of aerosols on waste incineration and their removal from emission gases has still not been studied in sufficient detail. We would like to mention the work of Zeuthen et al. [15], who studied aerosols isolated from emission gases of an incineration plant (with generation of 22 MW of electricity). Analysis of the composition of aerosols as a function of the type of incinerated wastes and incineration conditions showed that the content of fine particles in emission gases is roughly constant (PM$_{2.5}$ 252±21 mg m^{-3}) but increases considerably, when spent vehicle tyres, impregnated wood, food wastes containing sodium chloride (PM$_{2,5}$ 313, 320, and 431 mg m^{-3}, respectively) are incinerated. The aerosol particle size distribution follows a bimodal law, and, therewith, the fraction of particles smaller than 2.5 μm is 10 wt % in the total mass of solid wastes. The number of particles per unit volume of emissions, too, varies with the type of wastes (from 43 to 87 mln in 1 cm^3). Submicron aerosol particles largely consist of chlorides and sulfates. In all the samples studied, increased zinc and lead concentrations were found. In the particles smaller than 0.2 μm, the concentrations of toxic metals (Cu, Cd, Pt, Pb, and Zn) were especially high. The penetration through gas filters was estimated at ~2% for 0.5-μm particles and at 25% for 0.03-μm particles.

Production and consumption wastes contain largely organic substances, but inorganic substances (including water) are also present. The organic fraction of solid wastes is mostly lignocellulose (potential energy source). About 85% of dry solid municipal wastes can be incinerated and/or converted (plastics, metals, and glass) into a secondary raw material. Since the waste incineration ash contains highly toxic heavy metals and certain other toxic chemical substances in a concentrated state (the initial waste volume decreases about 10 times), the common practice of ash disposal or secondary use are unsuitable here. Special measures for detoxification of ash accumulated in incineration plants should be taken. At present many countries (Taiwan, Japan, USA, China, Brazil, and others) are developing a complex of measures for environmentally safe and economically efficient waste treatment, including safe utilization of toxic ash (its melting and fusion) [16, 17]. Surely, this requires additional capital, intellectual, and time commitments.

As mentioned above, the waste incineration residues (fly ash, cyclone and scrubber ash, and reactor ash) contain biotoxic components, and therefore, that are classed with hazardous wastes all over the world. At the same time, in view of the fact that in certain countries such residues contain much silicon, aluminum, calcium, iron, magnesium, sodium, and other elements, they found application as additives to building materials (concrete, cement, or gravel) [18]. The question of whether waste incineration wastes can be used in building materials, considered in terms of biological hazard to humans, is still open. We can add to that that in the overwhelming majority of countries there are no legal documents prescribing the necessity of controlling the quality and turnover of municipal solid waste incineration ash, and also certified

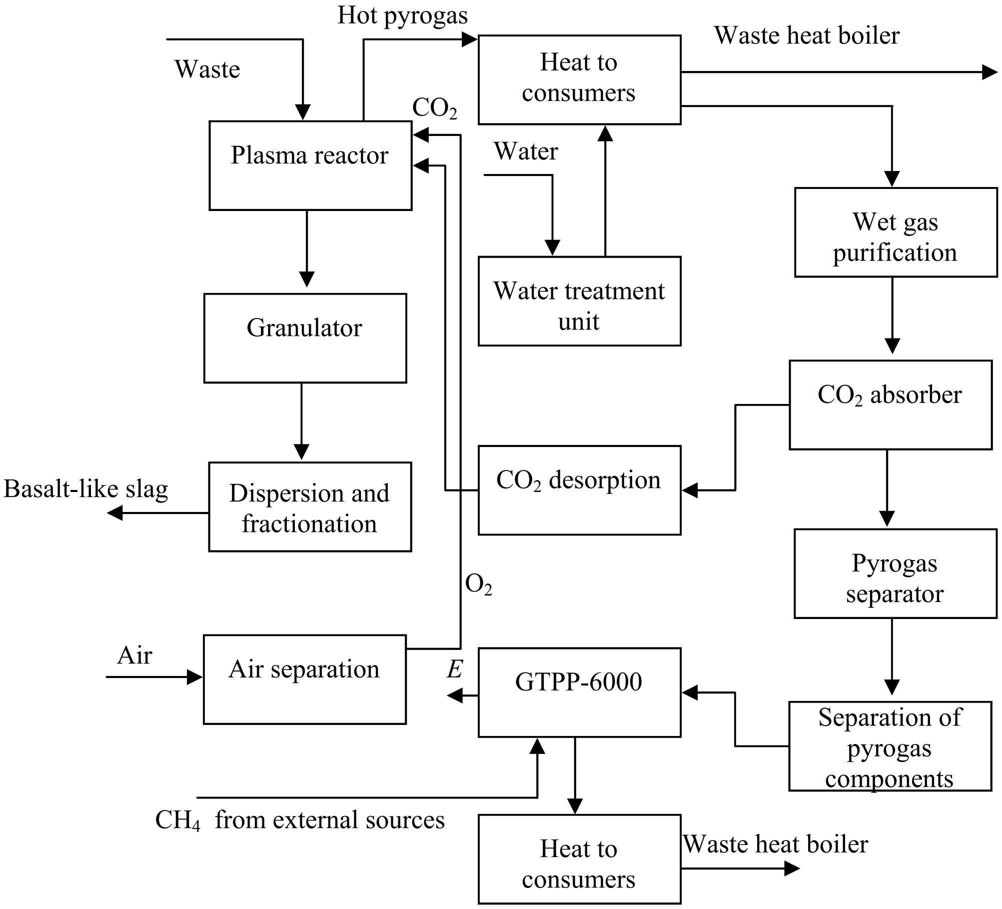

Fig. 1. Principal process scheme of a complex for high-temperature plasma conversion of solid wastes.

procedures for assessing its biological hazard and hazard to the environment in general [9]. Therefore, it is safe to state that without adequate toxicity assessment municipal solid waste incineration ash cannot be used as a secondary raw material both because of its potential hazard and because of the lack of the corresponding regulatory environmental law.

Thus, a conclusion can be drawn that the existing technologies at incineration plants fail to provide their environmental safety, in particular, modern gas purification systems are unable to trap finest particles (smaller than 0.1 μm) in emission gases and aerosols. Therefore, most effort should be focused on development of principles of treatment of production and consumption wastes, including medical wastes.

In the present paper we describe an innovative plasma technology of production and consumption waste treatment, commercialization of which makes it possible to approach the above-mentioned problems. The only inorganic residue after such treatment is a basaltiform slag. Even though it contains a certain quantity of heavy metals but they are present in an insoluble (inactive) form, which allows the basaltiform slag to be used as an environmentally safe building material.

The KORTEZ company has designed a complex implementing the technology of high-temperature plasma conversion of production and consumption wastes. The principal process diagram of this complex is presented in Fig. 1. Plasma burning of wastes (pyrolysis) is performed in a reactor equipped with a plasmatron which is a dc electric arc heater with controlled power of up to 600 kW. The plasma-forming gas or working body here is gas (air, carbon dioxide, methane, steam, or a mixture of gases. Carbon dioxide is separated from the products obtained by plasma technology and returned to the working cycle of the heater, which excludes or at least decreases release of this green-house gas to the atmosphere. Using different working bodies in the electric arc heater one can control the composition of gaseous products of plasma pyrolysis of solid wastes (pyrogas).

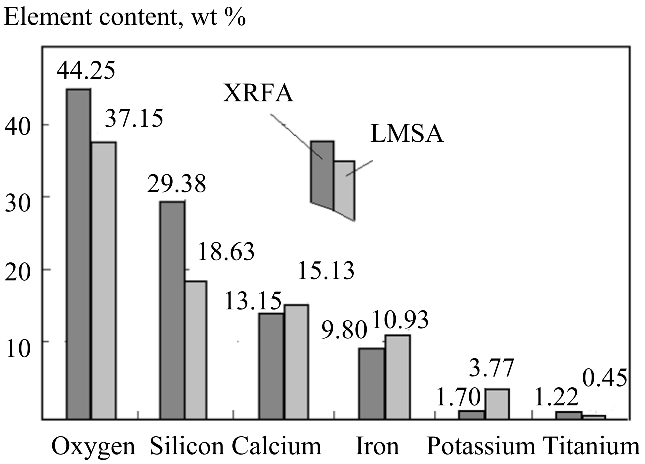

Fig. 2. Results of X-ray fluorescence analysis (XRFA) and laser mass spectral analysis (LMSA) of the glassy product of high-temperature plasma waste treatment.

Electric arc heaters allow the working zone, gasification zone, working zone walls to be heated to 5000 C, 2000°C, and 1800°C, respectively. Such high temperatures exclude formation of PCDD and PCDF (the average daily concentration of these compounds in emission gases is 0.01 ng/m^3, which is much lower than the existing standards). Plasma waste pyrolysis forms, in the lower part of the working zone, a basaltiform slag as a solid glassy product.

The experimental samples of this product were studied by means of thermal and X-ray fluorescence analysis.

Thermal analysis gave the following results: initial melting point of the glassy product 997.6°C, maximum melting point 1092.0°C, heat effect 400.4 J g^{-1}.

The results of X-ray fluorescence analysis are listed in Table 2. The results were checked by laser mass spectral analysis on an EMAL-2 instrument (Fig. 2) to show a fairly good (taking into account a non-uniform composition of the starting material for the glassy product) consistency with other analytical data.

Table 2. Results of X-ray fluorescence analysis of the solid glassy product of plasma waste treatment

Element	Concentration, wt %	Element	Concentration, wt %
Potassium	3.040	Copper	0.218
Calcium	23.57	Zinc	0.180
Titanium	2.190	Rubidium	0.011
Chromium	0.132	Strontium	0.151
Manganese	0.176	Silicon	52.66
Iron	17.57	Other components	0.084
Nickel	0.018		

Searching for possible application fields for the glassy product of high-temperature plasma conversion we performed an X-ray fluorescence analysis of similar materials: glass fiber as a spirally wound cylinder (ODE, Turkey), basalt samples from Ukrainian and Siberian deposits, and diorite (Table 3).

The elemental and thermal analyses of the glassy product allow us to envisage its possible application fields, namely, as a component of feed for manufacturing mineral cotton fiber and products from it (plates, rolling materials, mineral wool rolling mates, or mineral wool and spirally wound cylinders); as gravel for construction; spirally would heat-insulating cylinders for pipeline insulation.

The composition of pyrogas and, as a consequence, possible ways of its further treatment and utilization depend on the composition of waste, composition and intensity of feeding gas to electric arc heaters, as well as composition and intensity of feeding additives, in particular, steam, for the required compositions of pyrogas and solid glassy product, to the plasma pyrolysis stage.

To assess the effect of conditions of high-temperature plasma waste conversion on the quantitative composition of pyrogas, we calculated H_2, CO, CO_2, CH_4, and H_2O concentrations in the gas mixture formed with different working bodies in the electric arc heater. The concentrations of other hydrocarbon components (C_2H_6, C_2H_4, and higher hydrocarbons) and tars correlate with the CH_4 concentration in pyrogas. The calculations were performed under the assumption that the gas mixture is present in the thermodynamic equilibrium.

The equilibrium mixture composition was calculated as follows.

Elemental composition of the mixture (C, H, O) in the total flow entering the pyrolysis stage was preset. Using tabulated data we calculated formation enthalpy $\Delta_f H_i$ and entropy S_i for an ith component of pyrogas at temperature T:

$$\Delta_f H = aT + bT^2/2 + cT^3/3 + dT^4/4 - e/T + f,$$

$$S = a\ln(T) + bT + cT^2/2 + dT^3/3 - e/(2T^2) + g,$$

where a, b, c, d, e, f, and g are tabulated coefficients.

For the set temperature, the minimum Gibbs energy of the system $G(x_i)$ was calculated by the formula:

Table 3. Comparative analysis of certain construction materials

Material	Content of oxides, %									AM[a]
	SiO_2	Al_2O_3	CaO	MgO	$Fe_xO_y^{(tot)}$	Na_2O	K_2O	TiO_2	MnO	
Glassy product of plasma waste treatment	57.34	10.21	11.88	2.84	8.96	8.33	0.52	0.84	0.187	4.59
Glass fiber as spirally wound cylinder (ODE, Turkey)	62.52	2.40	8.14	4.12	0.09	25.43	0.06	0.05	0.02	5.29
Basalt										
Chelyabinsk Region (gray sample)	49.33	14.23	10.37	8.10	11.39	2.98	0.58	0.88	0.159	3.44
Chelyabinsk Region (light gray sample)	48.09	12.69	10.39	10.91	11.50	2.21	0.82	0.66	0.195	2.85
Ivano-Dolinsk deposit, Ukraine	50.83	14.89	9.10	3.83	14.84	2.62	0.68	3.08	0.19	5.08
Diorite, Yanzigit deposit	53.23	16.49	7.38	5.06	9.02	2.63	1.31	0.77	0.15	5.60

[a] (AM) Acidity module defined as the ratio of the total contents of acid and basic oxides (SiO_2 + Al_2O_3)/(CaO + MgO). The acidity module determines the material treatment technology.

$$G(x_i) = \Sigma_i \mu_i x_i = \Sigma_i[(\Delta_f H_i - TS_i) + RT \ln x_i]x_i,$$

where x_i is the molar (or volume) concentration of the ith component in the gas phase and m_i, chemical potential of the the ith component at temperature T. In searching for the minimum of the $G(x_i)$ function we posed restrictions on the x_i values, required for meeting the mass balance conditions for each of the elements (C, H, and O).

The calculation results (Fig. 3) showed the following.

With air as the working body in the electric arc heater, fairly much methane and tars are formed; the CO and hydrogen contents in pyrogase are roughly equal to each other. With CO_2 as the working body, little methane and tars are formed; the CO content is much higher compared to hydrogen over the entire temperature variation range we used in the plasma pyrolysis study. With steam as the working bode, little methane and tars are formed; the H_2/CO ratio gets close to 2:1, which is important, since just this ratio predetermines choice of technology for catalytic treatment of pyrogas.

When the working body is an equimolar mixture of water and CO_2, the H_2/CO ratio falls down to 0.85, while with the inert gas argon, it falls down further to 0.46.

Apparently, the optimum approach is to use a mixture of carbon dioxide and steam as the working body in the electric arc heater and then separate the components of pyrogas, isolate CO_2, and recycle the latter to the plasma process. The remaining part of CO_2 together with methane isolated from pyrogas can be used in the catalytic CO_2 and steam reforming processes to obtain syngas with the H_2/CO ratio of 2:1–3:1 and then used this mixture in the catalytic Fischer−Tropsch process to obtain a hydrocarbon fuel.

Steam and carbon dioxide reforming are performed in the presence of metal oxide catalysts at an elevated temperature:

$$CH_4 + H_2O = CO + 3H_2, \Delta H = +55 \text{ kcal mol}^{-1}, \quad (1)$$

$$CH_4 + CO_2 = 2CO + 2H_2, \Delta H = +62 \text{ kcal mol}^{-1}. \quad (2)$$

The resulting syngas is directed to the stage of Fischer−Tropsch hydrocarbon synthesis, which is performed in the presence of cobalt-containing catalysts at 120−140°C and 30 atm:

$$nCO + (2n + 1)H_2 = C_nH_{2n+2} + nH_2O. \quad (3)$$

The hydrocarbons formed under these conditions can be used as components of motor fuels. The mixture of saturated hydrocarbons contains a little of alkenes and other products. To drive reaction (3), the cobalt catalyst is promoted with zirconium, titanium, and manganese oxides. The selectivity of a promoted cobalt catalyst toward alkene formation is usually no less than 90%. The selectivity of the process is determined, apart from catalyst type, by conditions. Increased temperatures can cause heating of the catalyst and loss of its activity. The probability of formation of normal alkanes decreases and that of normal alkenes increases with increasing chain length of the hydrocarbons formed. Increased pressure in the system favors formation of heavier products, whereas increasing partial pressure of hydrogen in syngas

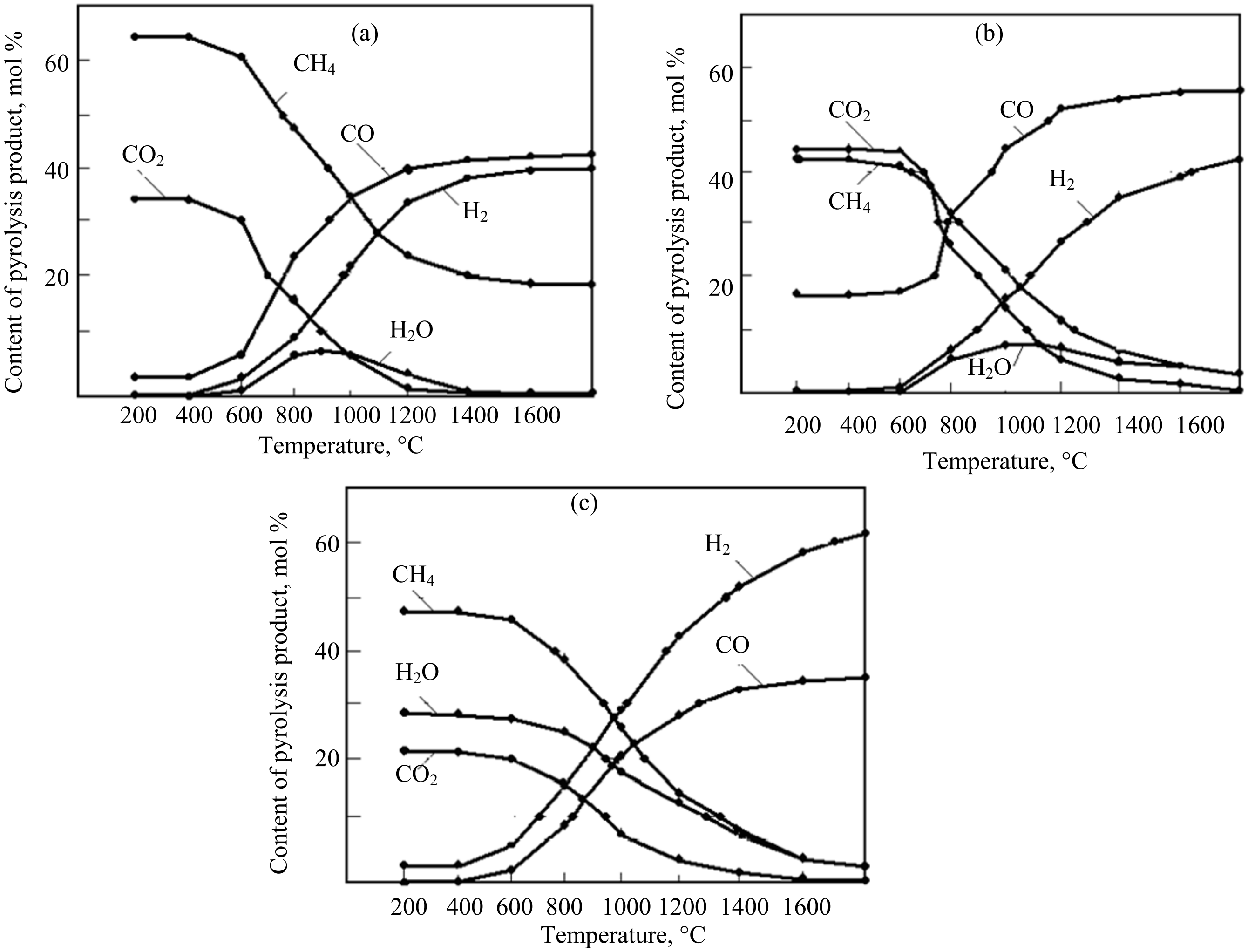

Fig. 3. Temperature dependence of the quantitative composition of gaseous pyrolysis products. Plasma-forming gas: (a) air, (b) carbon dioxide, and (c) steam.

favors alkane formation. The equilibrium *n*-alkanes/*iso*-alkanes ratio increases as the chain length in the hydrocarbons formed increases from 1.1 (butanes) to 19.2 (nonanes). The maximum yields of the kerosene and diesel fractions are 48% and 30%, respectively.

The process can also be implemented as a two stage Fischer−Tropsch hydrocarbon synthesis: the first involves production of hydrocarbon mixtures from syngas and the second, hydrocracking of the resulting hydrocarbon mixtures to obtain commercial products:

Table 4. Comparison of the incineration and plasma waste conversion technologies

Assessment criterion	Incineration	High-temperature plasma process
Formation and atmospheric emission of CO_2 (greenhouse gas)	Most CO_2 is emitted into the atmosphere	Most CO_2 is used in the plasma process and in CO_2 reforming
Contents of dibenzodioxins and dibenzofurans:		
pyrogas	7000−45000 ng m^{-3}	Formation of toxic compounds is excluded due to a high process temperature (above 1200°C)
ash	Contains toxic compounds	No ash is formed. The glassy residue that forms contains no hazardous admixtures
Possibility of production of motor fuel from pyrogas components	Production of motor fuel is economically reasonable	Allows production of motor fuel

diesel fuel and aviation kerosene. According to estimations, treatment of 2.5 ton/h of waste in the high-temperature plasma process with CO_2 as the working body in the electric arc heater, followed by steam or CO_2 reforming of Fischer–Tropsch products; the yield of hydrocarbons is about 300 kg/h, of which 70% falls on the C_5–C_{10} fraction, 29% on the C_{11}–C_{18} fraction, and 1% on the C_{18+} fraction. The kerosene and diesel fractions are isolated from the resulting hydrocarbon raw material by traditional methods.

As seen from Table 4, the high-temperature plasma waste conversion process offers a number of advantages over the traditional incineration technology.

It was shown above that the raw materials and working body for the electric arc heater strongly affect the composition of pyrogas. For an optimum-composition pyrogas, a mid-level elemental composition of the material fed to the plasma reactor should be maintained. To this end, appropriate additives are introduced either to the waste to be treated or to the plasma-forming medium via special channels.

The possibilities for controlling the process can be illustrated by the operation of the module for generating pyrogas for production of hydrogen and motor fuel components. Let us assume that the pyrogas obtained by treatment of solid wastes comprising largely municipal wastes, contains 28 vol % of CO, 42% of H_2, 14% of CH_4, 16% of H_2O and CO_2. If solid wastes of a different composition, say, heavy oil residues, are delivered for treatment, the pyrogas will contain more methane, other hydrocarbons, and tars, whereas the fractions of CO and hydrogen will, therefore, decrease. In this case, to increase the fraction of hydrogen in the pyrogas, water or wastes with enhanced moisture content can be added to the reactor; one more possibility is to increase the quantity of steam fed to the electric arc heater.

Thus, the evidence on the effect of the composition of waste and the nature and feed rate of the plasma-forming gas on the composition of the pyrogas can be used to develop a controlled high-temperature plasma waste treatment complex maximally adapted to the composition of the waste to be treated, as well as meeting requirements to the assortment of the final products (hydrogen, motor fuel, electric power, etc.).

A characteristic feature of the plasma technology is that it uses production and consumption wastes not only as a material to be destroyed, but also as a renewable source of raw material for production of energy components: power, hydrogen, or motor fuel. This approach underlies the new technology, endows it with a new "philosophy," and makes it economically more efficient and environmentally less hazardous compared with the technology of waste incineration at incineration plants.

At present the KORTEZ company has initiated preparation for constructing a pilot plant for plasma waste treatment in the Dmitrov District of the Moscow Region.

REFERENCES

1. Jean, P., Assefa, W., and Michel, C., *ACI Mater. J.*, 1996, vol. 93, p. 112.
2. Oh, J.E., Choi, S.D., Lee, S.J., and Chang, Y.S., *Chemosphere* , 2006, vol. 64, p. 579.
3. Zimmermann, R., Heger, H.J., Kettrup, A., and Nikolai, U., *Fresenius J. Anal. Chem* ., 2000, vol. 366, p. 368.
4. Riber, C., Fredriksen, G.S., and Christensen, T.H., *Waste Manag. Res* ., 2005, vol. 23, p. 126.
5. Maguhn, J., Karg, E., Kettrup, A., and Zimmermann, R., *Environ. Sci. Technol* ., 2003, vol. 37, p. 4761.
6. Kim, C.S., Bao, L., Okuyama, K., Shimada, M., and Niinuma, H., *J. Nanopart. Res* ., 2006, vol. 8, p. 215.
7. Jiang, W., Cheung, C.S., Chan, C.K., and Zhu, C., *Chinese Phys* ., 2006, vol. 15, p. 1864.
8. Zhao, L., Zhang, F., Wang, K., and Zhu, J., *Waste Manag.*, 2008, vol. 29, p. 1114.
9. Lin, K.-L. and Chen, B.-Y., *J. Hazard. Mater.*, 2006, A138, p. 9.
10. Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G. Jr., and Speizer, F.E., *New Engl. J. Med.*, 1993, vol. 329, p. 1753.
11. Delfino, R.J., Sioutas, C., and Malik, S., *Environ. Health Perspect.*, 2005, vol. 113, p. 934.
12. Lighty, J.S., Veranth, J.M., and Sarofim, A.F., *J. Air Waste Manag. Assoc.*, 2000, vol. 50, p. 565.
13. Yoo, J.I., Kim, K.H., Jang, H.N., Seo, Y.C., Seok, K.S., Hong, J.H., and Jang, M., *Atmos. Environ.*, 2002, vol. 36, p. 5057.
14. Thipse, S.S., Schoenitz, M., and Dreizin, E.L., *Fuel Process. Technol.*, 2002, vol. 75, p. 173.
15. Zeuthen, J.H., Pedersen, A.J., Hansen, J., Frandsen, F.J., Livbjerg, H., Riber, C., and Astrup, T., *Combust. Sci. Technol.*, 2007, vol. 179, no. 10, p. 2171.
16. Lin, K.L., *Cem. Concr. Res.,* 2005, vol. 35, no. 4, p. 979.
17. Lin, K.L., *J. Ind. Chem. Eng.*, 2005, vol. 11, no. 6, p. 834.
18. Mangialardi, T., Paolini, A.E., Polettini, A., and Sirini, P., *J. Hazard. Mater.*, 1999, vol. 70, nos. 1–2, p. 53.