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Catalytic Transformations of Gaseous Products of Plasma Treatment of Solid Wastes and Hydrocarbon Raw Materials

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Abstract—The layout of a technological process including catalytic steam and carbon dioxide reforming and Fischer−Tropsch hydrocarbon synthesis is presented. The inclusion of catalytic stages in plasma technologies provides the possibility to intensify conversion processes, enhance their depth, and obtain various gaseous and solid products.

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INTRODUCTION

The product of high-temperature plasma conversion of solid wastes is a low-calorific pyrogas which, after purification and mixing with natural gas, can be used as a raw material for power production. We consider it more promising to use pyrogas as a raw material for production of hydrocarbons and their derivatives, synthetic motor fuels, methanol, high-boiling paraffin hydrocarbons, etc. A possibility thus arises to organize a closed circuit cycle of hydrocarbon raw material and to involve an essential part of solid wastes into secondary use processes.

One of the problems associated with the application of the high-temperature plasma technology for production of synthetic motor fuels is to provide deep purification of pyrogas from gaseous admixtures formed at the stage of plasmachemical treatment of waste at 1500−2000°C in the reductive medium (hydrogen sulfide, ammonia, phosphine, arsine, hydrogen chloride, and others). Deep cleaning from these admixtures is necessary, since the version of the plasma technology, aimed at production of motor fuel components involves catalytic stages which are extremely sensitive to the above-mentioned admixtures. The necessity to include purification stages makes the catalytic version of the high-temperature plasma technology of solid waste treatment much more expensive. Moreover, pyrogas contains from 10 to 15% of water vapor and methane at a ratio corresponding to the composition of their equilibrium mixture at 1500°C.

Note that modern waste incineration technologies include the stage of gas purification from toxic components. Quite expensive catalytic technologies of gas purification from dibenzodioxins, dibenzofurans, and nitrogen oxides from gases [1–6] (CRI CATALYST) are known, which allow an almost complete purification (purification degree is not lower than 99.9%). The gas purification modules developed by the company are supplied as relatively small blocks (210×143×142 cm) providing a high throughput at a low gas pressure drop.

Catalytic Conversion of Gaseous Products of Plasma Solid Waste Treatment

The principal components of gaseous products (CO_2, CO, and H_2) obtained at the stage of plasma treatment of solid wastes can be involved, in a single process line, into catalytic reforming (steam or carbon dioxide) and Fischer−Tropsch hydrocarbon synthesis. The final products of this version of plasma technology are components of liquid fuel, as well as electric power and steam.

The process flow diagram of the plasma treatment of solid wastes, including these two catalytic stages, is presented in Fig. 1. Solid wastes by Line *1* are fed to

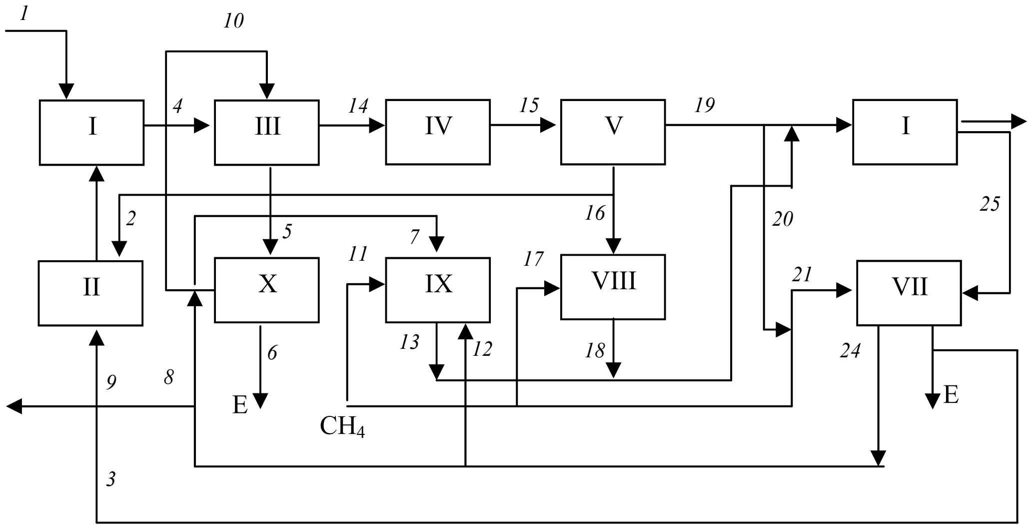

Fig. 1. Scheme of complex technology of plasma solid waste treatment and catalytic transformations of gaseous waste treatment products.

Blocks I and II for plasma treatment on plasmatrons installed at several height levels in a shaft reactor. The working gas in plasmatrons is carbon dioxide fed by Line *2* from the CO_2 isolation stage (Block V) [7]. Plasmatron is powered by Line *3* from the gas turbine installation (Block VII).

The hot pyrogas formed in the reactor is directed, by Line *4*, into a waste heat exchanger (Block III) where it cools down with steam generation. Part of steam by Line *5* is transferred to a gas turbine plant (Block X) to produce electric power (*E*) which is directed to a consumer by Line *6* {the consumer can be a plasmatron (not shown in the scheme)}. Another part of steam is directed, along Line *7*, to the steam reforming stage (Block IX). Moreover, more steam can be fed to this block by Line *12*. The remaining part of steam exits the system by Line *8* and is directed to a consumer by Line *9*. Steam condensate from the steam turbine plant is fed by Line *10* to the waste heat exchanger.

Methane is fed to the steam reforming stage from outer sources by Line *11*. The syngas generated at this stage is directed by Line *13* to the stage of Fischer−Tropsch synthesis of liquid fuel.

Steam reforming

$$CH_4 + H_2O = CO + 3H_2$$

is performed at ~650°C in the presence of metal oxide catalysts (most commonly Ni/Al_2O_3).

Cooled pyrogas along Line *14* goes to the purification stage (Block IV). The composition of a purified pyrogas before the CO_2 isolation stage is presented in Table 1. Further on pyrogas is directed by Line *15* to the CO_2 isolation stage (Block V). The process is performed using aqueous methyldiethanolamine as an absorbent. This absorbent offers a number of important advantages: (1) the high absorptivity with respect to CO_2 in a wide range of its partial pressures provides the required purification degree; (2) the lower vapor pressure of this absorbent prevents its loss with gas; and (3) the low viscosity of the absorbent solution ensures a good contact with gas. Moreover, the absorbent has a low corrosive activity, is resistant to foam formation, and exhibits a high thermal stability.

Table 1. Composition of purified pyrogas

Component	Content, wt %
CO	31–33
H_2	34–36
CH_4, C_2H_6, C_3H_8 (total)	5–7
H_2O	10–12
CO_2	12–15
N_2	≤ 3
O_2	≤ 1
Sulfur compounds (total)	≤ 100 ppm
Chlorine compounds (total)	≤ 50 ppm
Arsenic compounds (total)	≤ 50 ppm
Phosphorus compounds (total)	≤ 100 ppm

On contact of gas with the absorbent, a reaction of CO_2 with methyldiethanolamine takes place:

$$2(C_2H_4OH)_2CH\text{–}NH_2 + CO_2 + H_2O \\ \rightleftarrows [(C_2H_4OH)_2CHNH_3]_2CO_3.$$

As the pressure is decreased and the temperature is increased to 120°C, diethanolamine carbonate that forms decomposes with CO_2 evolution.

Part of the evolved CO_2 by Line *16* is directed to the CO_2 reforming stage (Block VIII). Methane is fed to the same block from outer sources by Line *17*. Syngas is formed at ~300°C in the presence of metal oxide catalysts:

$$CH_4 + CO_2 = 2CO + 2H_2.$$

The resulting syngas is directed to the stage of Fischer–Tropsch hydrocarbon synthesis (Block VI) along Line *18*.

The gas goes to the Fischer–Tropsch synthesis stage by Line *19*. Part of this stream can be directed, if necessary, by Line *20* to be mixed with methane fed by Line *21* to the steam turbine plant. The steam from the steam turbine plant is directed along Line *24* either to the steam reforming stage or to consumers. Methane and other light hydrocarbons obtained by Fischer–Tropsch synthesis are directed to the gas turbine plant by Line *25*.

The synthesis of hydrocarbons is performed at 120–140°C and 30 atm in the presence of cobalt-containing catalysts promoted by zirconium, titanium, and manganese oxides. Under these conditions, the major products are linear alkanes:

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

The resulting hydrocarbon raw material is separated into kerosene (48%) and diesel (30%) fractions. The side reactions in the Fischer–Tropsch synthesis are as follows:

hydrogenation of carbon monoxide to methane

$$CO + 3H_2 = CH_4 + H_2O$$

disproportionation of carbon monoxide

$$2CO = CO_2 + C$$

steam reforming

$$CO + H_2O = CO_2 + H_2$$

secondary reactions forming lower alkanes, alcohols, aldehydes, and acids, hydrogenation of alkenes, dehydrogenation of alcohols, hydrocracking of primary alkanes, etc.

In the waste treatment technology in focus, the first stage, plasma treatment, makes use of reactors combined with plasmatrons. The plasma reactor is operated at a reduced pressure, which prevents release of combustion products into the environment. The vacuum of the operating conditions is up to 1000–2000 Pa in the shaft reactor and up to 200 Pa in the melting furnace.

This variant of the plasma solid waste treatment technology offers such an undeniable advantage as environmental friendliness due to an almost complete conversion of waste into useful products (synthetic motor fuel, building materials from slag, electric power, and heat carrier) and absence of release of gasification products into the atmosphere.

To realize this technology, the complex should be located in the immediate vicinity of a natural gas–fueled gas turbine plant to ensure supply of methane to the reforming stage. The withdrawn methane will be compensated for by excessive jets of low- and medium-calorie pyrogas.

Instrumentation of the Catalytic Conversions of Gaseous Products of Solid Waste Treatment

Reactions for Steam and Carbon Dioxide Reforming

The reforming processes both are endothermic, heat is supplied in two ways: by internal heating (so-called autothermal reforming) due to the heat of combustion of part of the process gas in the catalytic zone [8] and by external heating of the catalytic zone [10–14]. An essential disadvantage of reactors with external heating is associated with essential heat losses. The constancy of the unit volume of the catalyst with respect to the reagent gas flow increases the pressure and decreases the rate of chemical reactions.

Effective catalytic reforming is provided by an annular plasma reactor (Fig. 2). In this reactor, the catalyst bed is arranged as a ring, due to which reagents move in a radial direction. The optimum ring width depends on several parameters. In particular, for the reaction to proceed in a preset temperature range, a slow temperature gradient in the catalyst bed should be maintained. Moreover, the volume of the unit catalyst layer should be so as to fit the equation: $S_1 \simeq S_2 = 2$ (see Fig. 2).

The reagents and catalyst are heated with a plasmatron fed by carbon dioxide (in the case of carbon dioxide reforming). Hot products of the plasmachemical conversion of CO_2 are mixed in the

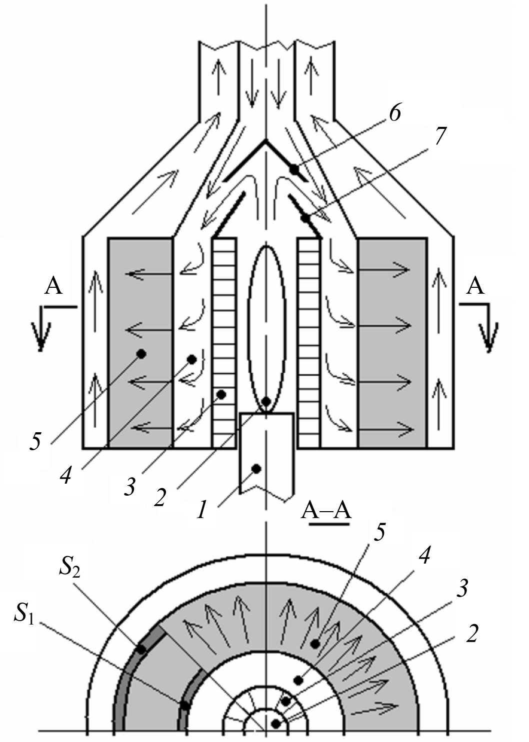

Fig. 2. Scheme of an annular plasma reactor for endothermic catalytic reactions: (*1*) plasmatron, (*2*) plasmachemical zone; (*3*) thermoinsulating (ceramic) wall; (*4*) buffer zone; (*5*) ring catalyst bed; (*6*) reflecting wall; and (*7*) deflecting wall.

buffer zone with the feed CO_2 and enter the reaction zone (realization of the internal heating technology).

The process temperature is controlled by the operation parameters of the plasmatron, dimensions of the plasmachemical zone (due to motion of the plasmatron along its axis), and ratio of the plasmachemical transformation products and the feed CO_2.

The performance of the process in this reactor can be enhanced by optimized heat exchange, radial motion of the reaction mixture, and involvement into the process of plasmachemical transformation products of the plasmatron working gas, which direct the process to major product formation.

Table 2 lists the results of calculation for carbon dioxide methane reforming, with account for the subsequent conversion of syngas into diesel fuel.

Reactors for Fischer−Tropsch Hydrocarbon Synthesis

By the Fischer−Tropsch synthesis is meant the following reaction sequence:

$$nCO + (2n + 1)\, H_2 = C_nH_{2n+2} + nH_2O,$$

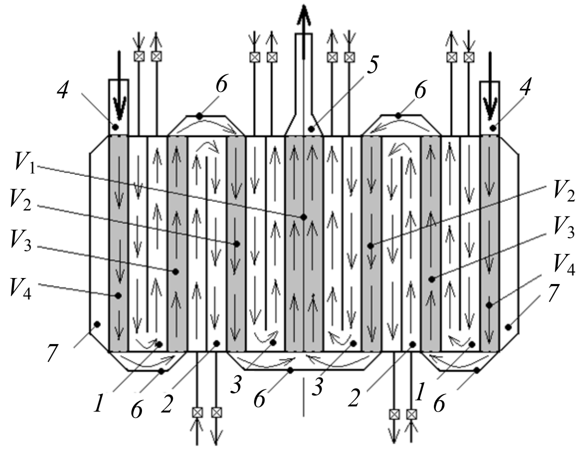

Fig. 3. Layout of an annular catalytic reactor: (V_1–V_4) catalytic sections; (*1*−*3*) sections with heat carrier; (*4*) inlet sleeve for syngas; (*5*) outlet sleeve for reaction products; (*6*) annular caps of catalytic sections; and (*7*) shell for feeding the cooling heat carrier.

$$nCO + 2nH_2 = C_nH_{2n} + nH_2O,$$

$$nCO + 2nH_2 = C_nH_{2n+1}OH + (n - 1)H_2O.$$

The reactions occur in the presence of iron- or cobalt-containing catalysts. The choice of catalyst is determined primarily by the composition of the syngas. At $H_2 : CO \geq 2$, the best results can be obtained with the cobalt-containing catalysts Co/Al_2O_3, Co/MgO, $Co/CoAl_2O_4$, Co/TiO_2, and others. The Fischer−Tropsch synthesis has been described in detail in [15–21]. Several types of reactors for the Fischer−Tropsch synthesis are known.

Fluidized catalytic bed reactor [22]. Reactors of this type have quite a complicated design and are very expensive to produce. The reaction zone of this reactor can accommodate a little of catalyst. Such reactors have not found wide commercial application.

Tubular reactor [23–28]. This is the most common type of reactors. In such reactors, the reaction rate is limited because of a poor heat removal and pressure drop.

Ring reactor (Fig. 3). Such reactors are almost free of the disadvantages of tubular reactors.

In an annular catalytic reactor, the reaction volume decreases about three times in going from one catalyst bed to another: $V_1{:}V_2{:}V_3{:}V_4 = 1{:}3{:}9{:}27$. Such catalyst distribution excludes effect of pressure drop on process selectivity and catalyst activity. The autonomous control of heat carrier temperature in the inner annular shells allows setting the required working temperature profile of the reactor, which minimizes local overheats and catalyst deactivation. Placing different-activity catalysts in the catalytic zones of the annular reactor favors a more stable thermal regime.

Suspension reactor (mixing reactor). In such reactors, the three phases of the reaction system, specifically gas, liquid, and catalyst, are all suspended due to vigorous mixing [29–35]. This type of reactors was given the name "slurry reactors." Note that Exxon Mobil has developed a multiphase slurry reactor for hydrocracking on a cobalt catalyst.

The slurry reactor should be combined with a block for production of finely dispersed catalysts by the plasma technology. The dispersion process involves exposure of coarse catalyst particles to a low-temperature plasma. Moreover, the low-temperature plasma reactivates deactivated catalyst particles. Plasma is generated by means of electrodes built-in into this block and delivering current to them (voltage 1.5–5.5 kV, frequency 0.25−0.8 MHz). The electrodes are linear in shape, the ratio of their length to electrode-to-electrode distance is (20−200):1. In this case, the reactor is tubular, and it has three standard elements (Fig. 4): One element includes inlet/outlet nippers for heat carrier and gas, liquid phase, and/or solid phase (catalyst) (Fig. 4, Section A); the second element includes linear electrodes and an inlet/outlet nipper for heat carrier (Section B); and the element includes no other equipment than an inlet/outlet nipper for heat carrier (Section C). The use of standard elements makes it possible to construct any plane-volume configuration of sections of the reactor block, appropriate for a concrete technology (rational use of the space of the working zone, convenient service, etc.). The circulation circuits for mixing of the reaction medium can be installed in any place of the reactor block. The presence of shells for heat carrier in each section and the possibility to deliver heat carrier into each section with any temperature allows setting any temperature profile over the reactor length.

Slurry reactors offer the advantage of isothermicity and lack of effect of intrinsic diffusion processes on the rate and selectivity of the catalytic reaction.

The disadvantage of slurry reactors is their low performance associated with a limited content of the catalytically active component in the slurry (no more than 250 kg of the catalyst in 1 m^3 of the reaction mixture). This limitation is explained by the fact that the gas content of the slurry and its dynamic viscosity depend on the catalyst concentration: Increasing concentration leads to increased vescodity of the liquid phase, which decreases the gas content of the slurry. The optimal catalyst concentration is 20−25 wt %. A developed gas−liquid interface can be maintained if the slurry reactor has a sufficiently large height (more than 20 m), which makes they impossible to use on mobile platforms and at facilities. Another disadvantage of slurry reactors relates to the ideal mixing mode realized in reactors of this type, which is less favorable for catalyst performance compared to the ideal expulsion mode characteristic of reactors with a fixed catalyst bed. Furthermore, in the case of slurry reactors, the process scheme should include a technically complicated stage of separation of catalyst particles from reaction products.

Table 2. Input data and principal results of calculations for carbon dioxide reforming and diesel production from syngas

Parameter	Value
Electric power of plasmatron, kW	600.0
Consumed electric power, MW h/year	5382.0
Operational costs (including costs of electric power and CO_2), thsd. roubles/year	4949.7
Cost of natural gas, thsd. roubles/year	6728.4
Heat capacity of plasmatron, Mcal/h	576.3
Specific heat capacity of natural gas, kcal/(kg deg)	0.94
Specific heat capacity of CO_2, kcal/(kg deg)	0.27
Reactor temperature, °C	1200
CO_2 consumption, kg/kg natural gas	2.75
CO_2 flow through plasmatron, kg/h	955.6
Natural gas flow, kg/h	267.9
CO_2 flow, kg/h	687.7
Syngas flow, kg/h	1004.6
Residual CO, kg/h	502.3
Calorific power of residual CO, kcal/h	1213363.5
Production of diesel fuel, ton/year	1452.1
Diesel fuel sales revenue, thsd. roubles/year	19893.1
Total profit, thsd. roubles/year	8215.0

Catalytic Stages of Plasma Technologies of Hydrocarbon Raw Material and Waste Treatment

At present there is a disaster in the world with utilization of oil-containing wastes, liquidation of oil sludges and acidic tars, and cleaning up oil-contaminated lands.

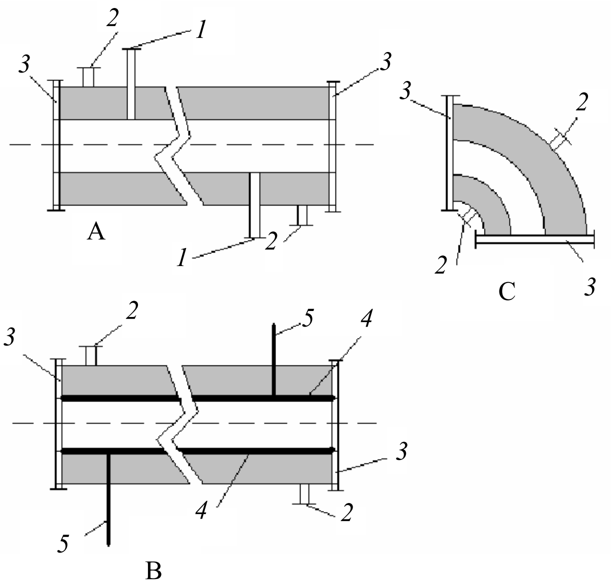

Fig. 4. Principal elements (sections) of multiphase slurry catalytic reactor: (*1*) gas, liquid, and/or catalyst inlet/outlet nippers; (*2*) heat carrier inlet/outlet nippers; (*3*) connecting nippers; and (*4, 5*) linear electrodes.

Liquid wastes containing more than 14% of oil products are generally incinerated. When the content of oil products is less than 14%, microbiological cleaning is applied.

However, until now no acceptable solution for the most complicated problem, specifically, cleaning up repeatedly oil-contaminated lands (at the territory of car service centers, sea ports, railway depots, , bulk plants, etc.), as well as utilization of sediments from oil tanks, collection ponds, and ground waste pits, which represent a solid phase containing paraffins, acidic tars, sulfur, sand, clay, and mechanical admixtures, as well as heavy metals (lead, cadmium, zinc, and others). Now such wastes are suggested to utilize by thermal treatment to obtain a dry, decontaminated carbon-containing product used as a raw material for building materials and asphalt-concrete mixtures, as well as condensate and gas, which are used as a fuel for the plant itself. However, such solution of the problem cannot be considered satisfactory, since solid pyrolysis residues contain heavy metals, they are unsuitable for commercial application and should be buried.

Extraction of oil from sediments is unreasonable in view of the high cost and low oil content (on average, 5–8%).

Utilization of acidic tars which are wastes of sulfuric acid treatment of certain oil products, such as lubricant oils, is a problem for many countries. Acidic tars contain resinous substances, organic compounds, heavy metals, sulfur, polymers, as well as up to 70% of sulfuric acid dissolved in water. Acidic tars are generally stored in open pits, which is dangerous for the environment. Most utilization technologies limit to regeneration of sulfuric acid from acidic tars and burning of neutral residues or to neutralization with limestone followed by burning on thermal power plants. Such treatment produces highly toxic atmospheric emissions.

The most rational approach to the problem of utilization of oil-containing wastes and/or heavy oil fractions is their combined pyrolysis with solid domestic wastes. However, this technology does not exclude environmental pollution with heavy metals, dibenzodioxins, and dibenzofurans.

The mentioned environmental problems can be solved by using plasma technologies for combined treatment of oil-containing wastes and/or heavy oil fractions with solid domestic wastes.

Plasmachemical technologies make possible higher degrees of treatment (raw material conversion is 96–98 wt %) and higher degrees of conversion of organic wastes into unsaturated hydrocarbons (more than 75%), can use heavy oil fractions (kerosene and diesel) as a raw material, involve less branched chemical processes, and include less stages.

The processes of plasmachemical treatment of hydrocarbon raw materials, including oil-containing wastes and/or heavy oil fractions, can be classified by the following principal characteristics.

(1) Phase state of the raw material subjected to plasmachemical treatment: gaseous hydrocarbons and their mixtures, liquid hydrocarbons and their mixtures, solid hydrocarbons, mixtures of liquid and solid hydrocarbons, and mixtures of gaseous, liquid, and solid hydrocarbons.

(2) Plasma-forming gas (plasmatron working medium): oxygen-containing gas, including air, water vapors, gaseous hydrocarbons, hydrogen or hydrogen-containing gases, inert gases, including mixtures of the above-listed gases.

(3) Presence or absence of catalyst.

In accordance with this classification, below we provide a description of plasma technologies of treatment of hydrocarbon raw materials with different phase compositions.

Plasmachemical Treatment of Gaseous Hydrocarbons

Hydrogen plasma pyrolysis of natural gas produces an acetylene-containing pyrogas [36]. Acetylene is hydrogenated, without isolation from pyrogas, to ethylene in the presence of a catalyst in a liquid solvent medium (three-phase catalytic system). The resulting ethylene is isolated by low-temperature rectification. Part of the hydrogen-containing gas formed by pyrolysis is returned to the pyrolysis stage, and its excess is used at the gas turbine plant. Liquid acetylene hydrogenation products, too, are returned to the pyrolysis stage as a secondary raw material.

A version of the plasmachemical pyrolysis of gaseous hydrocarbons with a mixture of gaseous hydrocarbons and pyrogas (after the isolation from it of hydrogen and acetylene) as a plasma-forming gas was suggested [37].

Plasma technologies are recommended for conversion of gaseous raw materials (petroleum gases, gas condensate, and other hydrocarbons) into solid products [38]. The plasma-forming gas here is an inert gas or a gas mixture. The hydrocarbon raw material is subjected to plasmachemical pyrolysis and plasma polymerization, and the resulting solid polymerization products are withdrawn from the plasma gas jet. The gas jet is purified from unreacted hydrocarbon gases, and the remaining gas is compressed and returned as a plasma jet to the stage of hydrocarbon plasma pyrolysis. The process provides a high degree of conversion of the hydrocarbon raw material into solid hydrocarbon polymers.

A plasmachemical process allowing conversion of methane into ethylene, acetylene, and other lower olefinshas been reported [39]. The conversion of methane is accomplished in two stages: the first stage involves heating to 1530−1830ºC for 0.01−0.02 s, and the second involves exposure of a hot mixture of primary conversion products to a pressure of 2−5 MPa in an adiabatic mode for 0.5−0.1 s. Further on the reaction products are quenched. In doing so, the temperature range used at the first stage of methane conversion is maintained by external power supply. At the first stage the mixture is heated in a hydrogen plasma. This technology makes possible direct methane conversion (conversion 88.4%) to obtain, among pyrolysis products, ethylene (67.4%) and acetylene (9.1%).

To produce acetylene by the plasmachemical pyrolysis of hydrocarbons [40], the plasma-forming gas (carbon-containing tail gases) is diluted with steam. The C/O molar ratio in the mixture is 1:(1−1.5), preferably 1:1.1.

Plasmachemical Treatment of Liquid Hydrocarbons

Conversion of gas condensate can be performed in a gas condensate plasma [41]. The products are quenched in a liquid hydrocarbon with concurrent throttling followed by repeated quenching in a liquid hydrocarbon.

Plasmachemical production of acetylene and ethylene from a liquid hydrocarbon raw material has been reported [42]. Liquid hydrocarbon are subjected to plasmachemical pyrolysis in a plasma-forming medium (technical hydrogen or a hydrogen−methane mixture), pyrogas is purified from soot and tars, compressed, and dried, after which it is separated from C_3, C_4, and higher (acetylene homologs) hydrocarbons.

Plasmachemical Treatment of Heavy Oil Residues

Heavy tars containing emulsified water and coke are treated by plasmachemical pyrolysis followed by quenching of products and their separation [43]. The raw material is preliminarily homogenized. Pyrolysis products are quenched, freed from acetylene by catalytic hydrogenation, and condensed. Uncondensed methane−hydrogen fraction was separated and used as a plasma-forming gas and/or boiler fuel. This technology makes it possible realization of low-waste closed-loop complex waste treatment due to utilization of environmentally dangerous wastes of petrochemical and chemical industries, to use more efficiently the raw material, and to increase the yield of the final product.

Heavy oil residues can be subjected to plasmachemical pyrolysis in a hydrogen-containing gas jet to obtain pyrogas and technical carbon, and also to convert sulfur compounds into hydrogen sulfide [44]. Pyrolysis products are purified from technical carbon followed by precipitation of rare metals. The isolated hydrogen sulfide is dissociated in an MW plasma to give polymeric sulfur and hydrogen, and the latter is returned to the pyrolysis stage. The purified gases are used to synthesize motor fuel. This technology allows extension of the raw material base, a more efficient treatment of heavy oil residues, and a more efficient use of the raw material.

In the course of hydrocracking of heavy hydrocarbon fractions [45], the heavy hydrocarbon fraction preheated to 360−370°C is subjected to hydrogen plasma treatment in a reactor in oxygen-proof conditions. Plasmatron equipped with a nozzle is installed in the upper part of the reactor, and the lower part of the reactor is equipped with a sleeve with a jet nozzle for feeding heavy hydrocarbon fractions. The jet nozzle is located so that the distance between the plasmatron nozzle to the upper part of the jet nozzle is regulated. Such construction makes it possible to simplify the technology of hydrocracking of heavy hydrocarbon raw material. Therewith, the process efficiency is enhanced by controlling the degree of cracking of hydrocarbon molecules. Furthermore, the reactor can be operated in two process modes to produce gas or light liquid fractions.

The patent [46] describes a plasmachemical hydrocracking process. The heavy hydrocarbon fraction preheated to 60−350°C is exposed to high-temperature plasma in oxygen-free conditions to crack long-chain hydrocarbon molecules into smaller fragments. The subsequent hydrogenation of the latter in the reaction zone forms light hydrocarbons.

Kashapov et al. [47] have described a process of treatment of high-viscosity oil residues, specifically fuel oil and tar. The enhanced depth of treatment of heavy oils and fuel oils is ensured by that the profound destructive pyrolysis is performed in a plasma jet of an inert gas, hydrogen containing gas, or nitrogen. This process offers unique possibilities in terms of reaction selectivity and features a simple-to-implement technology. Reaction intensity depends on many factors (gas and raw material temperature, heat carrier-to-raw material molar ratio, heat and mass exchange, etc.).

Kinetics of a plasmachemical process implemented in a plasma generator with compressed airflow through the arc and vortex arc stabilization were studied. Oil heated to 80°C was fed to the plasma zone exit (plasma temperature 2730−5730°C). Gas (inert gas, hydrogen-containing gas, nitrogen) heating in the electric arc occurs primarily due to the energy released in the arc column. Mixing with the plasma-forming gas, the reaction mixture passes through the reaction chamber and enters the quenching chamber. The resulting product is directed to a large-volume chamber (for composition equalization) and further to the final cooling zone. The final gaseous product contains primarily ethylene and acetylene hhydrocarbons, as well as molecular hydrogen and fine soot.

Plasmachemical Treatment of Solid Waste and Mixture of Solid and Liquid Wastes

A process for manufacturing acetylene from organic solid wastes by plasma pyrolysis of ground raw material mixed with steam [48].

The utilization of oil pit sludge [49] is based on the plasmachemical treatment in the presence of hydrogen preheated to 3000−4000°C to form C_2−C_4 unsaturated hydrocarbons. Before plasmachemical treatment the sludge is diluted with crude oil (weight ratio 1:0.25) and heated to 90−95°C. The technical result was the development of a small-sized, high-performance, intertialess, and environmentally friendly technology for sludge treatment.

Gasification of solid carbon-containing materials [50] allows production of syngas from plastic wastes. The process includes feeding a ground raw material and steam plasma, their mixing in a molten pool, with the subsequent plasmathermal gasification of the raw material and removal of products. The process is implemented in a plant including a plasmathermal reactor, double-jet plasmatron, control inlet nippers for dispersed raw material and steam, and outlet nippers for syngas and solid particles. The plasmachemical reactor comprises plasma and cyclone reactors linked with a gas pipe. The technology enhances the economic efficiency of the plasmachemical production of high-quality syngas in a compact plasmathermal reactor in a single process stage.

In the present review we do not tough upon plasma gasification of coal. The information on the present state of this problem can be found in [51−60].

Plasma Catalytic Treatment of Hydrocarbon Raw Material

A technology for purification of oil fractions from organic sulfur compounds [61] by high-temperature pyrolysis in the presence of hydrogen and a catalyst has been described. The process is implemented in a plasmachemical reactor. One part of a dispersed catalyst is introduced, together with raw material, into the working zone of the reactor, and the other part is introduced into the quenching chamber as a suspendsion. The process provides deep purification of oil fractions and generates less hazardous wastes.

Utilization of oil sludges by plasma treatment in the presence of catalysts has been reported [62]. Oil sludges as dispersed combustible water−fuel compositions are exposed to a catalytically active air electric change plasma at an average temperature 1200−6000ºC for 10^{-5}−10^{-3} s; the content of ultrafine catalytically active materials (obtained in the process of plasmacatalytic utilization of oil sludges) in the reaction mixture is 0.01−1.0 wt %. The plasmacatalytic reactor comprises a plasma generator, reaction chamber, nozzle, and sleeves for feeding raw materials and removing products. The installation realizing this process is small-sized, compact, and mobile. The process is economically efficient: high specific performance, low specific power consumption for utilization, generation of additional heat energy for industrial and domestic needs. It offers substantial advantages in terms of environmental safety: low contents of pollutants in purified emission gases, lack of organic pollutants in solid utilization products, and lack of contaminated wastewater.

The patent [63] describes a process for manufacturing ethylene, based on plasma-catalytic methane conversion. The process involves catalyst activation with MW irradiation and generation of a non-equilibrium "cold" MW plasma.

A combination of a plasmachemical and catalytic pyrolysis processes was realized in a process for manufacturing acetylene from natural gas [64]. In this process, an activated additive (potassium carbonate powder) is introduced into a hydrogen plasma jet, and pyrolysis occurs when the hydrogen plasma is mixed with natural gas jets. The yield of the final product (acetylene) in this process is slightly increased, but it activating additives are not consumed completely: Plasma jet containing additives gives an insufficiently uniform mixture with natural gas. This decreases the efficiency of plasmachemical pyrolysis and increases specific power costs and additives consumption.

A technology of catalytic plasmachemical pyrolysis of oil and oil residues has been suggested [65]. A finely dispersed catalyst, irrespective of its aggregation state, is preliminarily dispersed with raw material. The spent catalyst after separation of pyrolysis products is regenerated and returned to the pyrolysis stage. The pyrocondensate is used to isolate C_2–C_4 unsaturated hydrocarbons and gasoline and methane–hydrogen fractions, after which the latter is returned to the stage of plasmochemical pyrolysis.

The disadvantage of this technology is a complicated catalyst contour, which is associated with the necessity to isolate the catalyst and return it to the process.

Quite promising is a process of treatment of oil and/or oil residues, based on plasmachemical pyrolysis of a homogenized mixture of a hydrocarbon raw material and finely dispersed catalyst. Pyrolysis occurs in low-temperature plasma formed in the interelectrode space (interelectrode voltage 1.5–5.5 kV, current frequency 0.25–0.8 MHz).

This process allows oil and/or oil residues to be treated in the presence of solid wastes (20–7 wt %). In this case, a homogenized mixture is subjected to plasmachemical pyrolysis at 200–400°C.

Pyrolysis products are quenched in a quenching unit, and the pyrocondensate is filtered and separated to isolate C_2–C_4 unsaturated hydrocarbons, gasoline fraction (part of which is directed for preparing a three-phase catalytic system, and methane–hydrogen fraction (part of which, too, is used for preparing the catalytic system).

This technology offers the advantages of using more active, finely dispersed catalysts, as well as simplicity, since it does not include the stage of catalyst isolation and recycling.

CONCLUSIONS

It is quite obvious that the inclusion of catalytic stage in high-temperature and plasma waste treatment is a rational approach. Catalytic stages in plasma technologies make it possible to considerably intensify the processes, increase the depth of waste treatment, and obtain technically valuable gaseous and solid products.

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