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Energy of low-temperature plasma in the processes of thermal conversions of carbon-containing medium

Anatolii Bulat[1], Leonid Kholiavchenko[1], Serhii Oparin[1,3], Serhii Davydov[1], Oleksandr Zhevzhyk[2] and Iryna Potapchuk[1]

[1]Institute of Geotechnical Mechanics named by N. Poljakov of National Academy of Sciences of Ukraine, Simferopolska, 2a, Dnipro, 49005, Ukraine
[2]Dnipropetrovsk National University of Railway Transport named after Academician V. Lazaryan, Lazaryan Str., 2, Dnipro, 49010, Ukraine

[3]Corresponding author: oparinsa1977@gmail.com

Abstract. One alternative for solving negative environmental impact is to use alternative renewable energy sources. However, technology is evolving and nowadays it cannot meet the needs of emerging economies. A promising direction in the field of clean technologies is the preliminary preparation of carbon-containing media of various origins by thermoconverting them into a gaseous state in high temperature fields. The analysis of the existing autothermal and allottermic technologies of gasification of carbonaceous media is given in the work. The advantages of allottermic technologies of high-temperature transformations under the action of arc plasma with steam oxidizing medium are presented. This method includes plasma formation processes, which combine in time and space thermal transformations and the generation of oxidant from water. The results of theoretical studies of the carbon-containing media plasma transformation process is presented in the article. The regularities of the temperature of steam-plasma transformation process influence on the qualitative and quantitative indicators of the obtained gas phase taking into account the medium elemental composition are established. Comparison of the cost indicators of production of synthetic motor fuel from natural gas by the known companies and from coal by steam-plasma conversion to gas is carried out.

1. Introduction

In the energy balance of developed countries, a significant share is occupied by oil and natural gas, the reserves of which are quite limited. According to experts [1] production of fossil fuels will peak around 2030 and return to current levels by 2050. Market share of fossil fuels will decrease by 17% overall. In these conditions, the world's energy should definitely be reoriented from oil and gas to alternative and renewable energy sources.

Ukraine's industry, which focuses mainly on oil and gas, is one of the most energy-intensive in Europe. According to the International Energy Agency [2], the energy intensity of Ukraine's GDP (gross domestic product) at purchasing power parity in US dollars is 2…3 higher than in developed European countries. The remaining oil reserves are limited by the complexity of their occurrence at great (over 5…6 thousand m) depths, and the production of own gas is difficult and insufficient. At the same time, Ukraine has significant reserves of renewable energy sources and solid combustible minerals. Reserves of peat, hard and brown coal of various metamorphic grade amount to 22.2 billion tons, including 2.6 billion tons of brown coal and 19.6 billion tons of low-grade metamorphism coal [3]. Such coal occurs at shallow depths. It is mined in favorable geological conditions and has a low cost. Thermal energy is successfully used for its extraction [4, 5], including green low-plasma energy [6]. However, all these coals are environmentally "dirty" energy sources. In the process of their extraction, enrichment and processing, a huge amount of waste is formed. These wastes are mainly stored in dumps, settling tanks and released into the atmosphere and reservoirs. They are practically unclaimed, occupy large fertile land areas, create soil erosion and pollute the environment. Processing by direct combustion of such carbonaceous media is a serious environmental regulations violation and increasing volumes of such processing will turn into catastrophic. Since there are no natural environmentally friendly energy resources that could fully meet the needs of energy consumption and the environment, the "dirty" energy carriers should be synthesized into clean energy sources. They should meet the following requirements: not to create pollution problems; to be competitive and available on the market of natural fuels. Renewable energy sources fully meet these requirements, but they are still in development and today cannot fully meet the developing economies needs. It is obvious that the existing technology of direct combustion should be replaced by new multi-purpose, waste-free, energy-saving, environmentally friendly technologies for converting "dirty" energy commodity into environmentally friendly fuel. It can be solved by preliminary preparing of carbon-containing media of various origins for common and safe use by thermoconverting them into a gaseous state. Considerable experience, which is based on autothermal technologies, has been accumulated in this direction. All these technologies are based on the combustion of gasified fuel part to accelerate and support the endothermic reactions of the conversion process [7]. Autothermal technologies are characterized by low temperatures (1400 ... 1500 K) and low heat flux density in the reaction space. Such parameters can not provide a sufficient level of harmful and toxic compounds destruction, high rate of thermal conversion and the degree of carbon processing. Thus complex processing of raw materials is practically excluded. Direct combustion of fuel causes a number of disadvantages of these technologies: low process productivity; pollution of the gas phase by fuel combustion products; pollution of the condensed phase by residual carbon; cumbersome, expensive and expensive equipment, especially for the production of oxidant; significant (up to 10...20 %) CO_2 emissions into the environment when using steam-oxygen blast; in the gas phase, nitrogen can reach 60 % when using air as an oxidant. These shortcomings and high investment in the construction of autothermal gasifiers prevent the widespread use of these technologies.

Allottermic technologies of high-temperature transformations can be an alternative to autothermal technologies. For allottermic processes of the carbon-containing media (CCM) into a gas conversion, the energy adds into the reaction space in the required quantity and quality from the outside (from an independent source). Among such sources could be considered low-temperature plasma energy flow, arc discharge energy, atomic energy, energy of light radiation, electron beam energy, etc. These processes use the low-temperature plasma energy. They are the most elaborated scientifically and have developed material base.

The aim of the work is to calculate the equilibrium composition of the processes of anthracite (carbon-containing) with different oxidizing media, to determine the energy consumption of these processes and to build a technological scheme for converting carbon-containing media with low-temperature plasma energy.

2. Methods

The calculation of the equilibrium of a multicomponent thermodynamic system is carried out according to the principle that for equilibrium the entropy of the system reaches its maximum.

For the reaction of interaction of coal and water steam (H_2O) at temperatures of 500...4000 K the entropy of the system is the sum of the entropy of the gas phase S^{I} and the entropy of the condensed (solid) phase S^{II}:

$$S = S^{\mathrm{I}} + S^{\mathrm{II}}. \tag{1}$$

For the gas phase [8]:

$$S^{\mathrm{I}} = \sum_{i=1}^{k}\left[S_i^0 - \frac{1}{n_i}\int_{P_0}^{P_i}\left(\frac{\partial v}{\partial T}\right)_P dP\right]n_i\,, \tag{2}$$

For an ideal gas with the equation of state $P_iV=n_iRT$ relationship (2) can be written as follows:

$$S^{\mathrm{I}} = \sum_{i=1}^{k}\left[S_i^0 - R\cdot\ln\left(\frac{R\cdot T\cdot n_i}{vP_0}\right)\right]n_i\,, \tag{3}$$

where S_i^0 – the standard entropy of the i-th component at temperature T and pressure P_0 = 101325 Pa, J/(mol·K); v – specific volume of the entire system, m^3/kg; $R{\cdot}T{\cdot}M_i/v = P_i$ – the partial pressure of the i-th gaseous component for equilibrium, Pa; R = 8.314 J/(mol·K) – gas constant; n_i – the content of gas phase components (i = 1, 2,...,k), mol/kg.

For the condensed phase:

$$S^{\mathrm{II}} = \sum_{j=1}^{m} S_j^0 n_j\,, \tag{4}$$

where S_j^0 – the condensed phase entropy (j = 1,2,…,m) per 1 mol of individual substance, J/(mol·K); n_j – the number of moles in 1 kg of working gas.

The values of standard entropies were determined depending on the temperature according to [9].

Thus it is necessary to find the maximum value of entropy ($S \rightarrow$ max), where the coordinates of the extremum are the number of moles of individual substances. The gradient descent method was used to determine the maximum value of entropy [10].

3. Results and discussion

Plasma energy sources differ in versatility of the properties of the raw materials; selectivity of useful product components; environmental safety; rational use of raw materials; high rates of chemical reactions and process efficiency for the flow; low metal capacity of the equipment [7]. This way of thermal interaction comprehensively meets the technical requirements as well as environmental indicators of the transformation process and the quality of the useful product.

Incoming of such energy can be carried out by separate and combined schemes, which differ in the nature and rates of transformation reactions, the sustainability of the processes of plasma formation and the medium transformation, the energy consumption of the process, the complexity of design solutions. Separate schemes distinguish by separated in space and time processes of plasma formation and thermal transformation of the medium within streams. The main features of these schemes are as follows: double energy conversion and predominantly convective heat transfer in media transformation processes.

The paper presents combined schemes in which the processes of plasma formation, the medium transformation and the oxidant generation are combined in time and space under the action of the arc discharge energy. In this case, the radiation component of the heat flux dominates the heat exchange processes, which accelerates the reaction processes, and the arc discharge energy without additional transitions is converted into thermal energy, which affects on the medium and generates oxidant from water.

Temperature is the main factor that shapes the process of transformation of the medium into a gaseous state. Previous studies established [11-13] that it is optimal to heat up a polydisperse particle regardless of its size to a temperature range T = (1800…2000) K. Within this temperature range the maximum yield of the gas phase and its calorific value are observed, and the degree of carbon conversion reaches 100 %.

The results of research in the form of the established dependences of the quantity and composition of the gas phase, energy consumption of the process and product quality indicators on the temperature in the reaction space under the influence of steam plasma energy are shown in figures 1, 2.

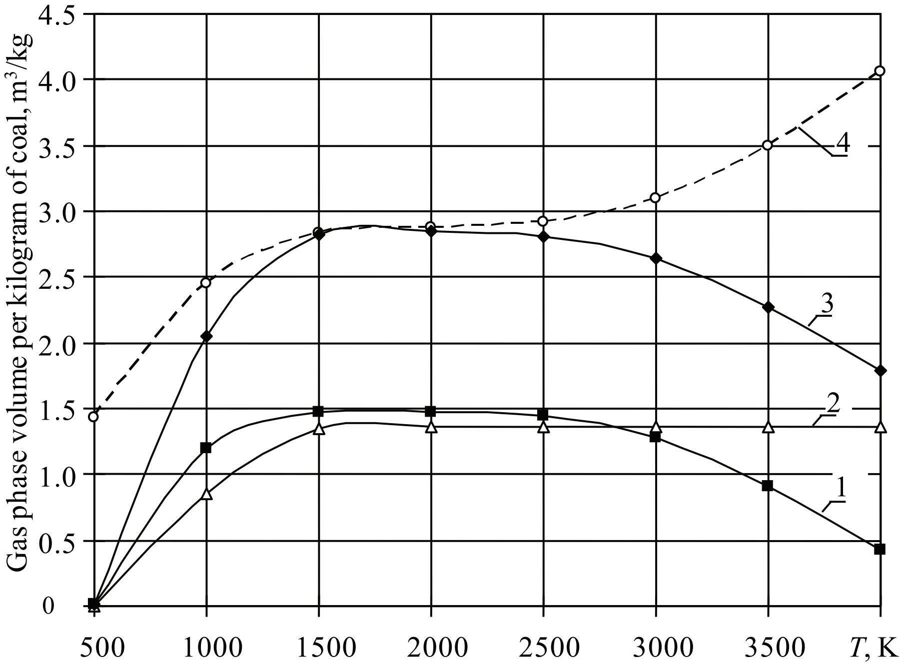

Figure 1. Dependencies of indexes of the process of carbon-containing medium transformations under the impact of steam-plasma energy: 1 – H_2 yield, 2 – CO yield, 3 – CO + H_2 yield, 4 – total volume gas phase.

Within a steam oxidizing medium and a temperature of 1800 K, the specific yield of gas is reaches its maximum value 2.67 m^3/kg of coal, which is 50…55 % higher than in oxygen blast. The energy component of the gas (H_2+CO) reaches 98…99 %, saturation with hydrogen by 50…55 % from the oxidizing medium, while the hydrogen oxide number value (H_2/CO) exceeds 1, which is positively affect the technology of liquid hydrocarbons chemical synthesis.

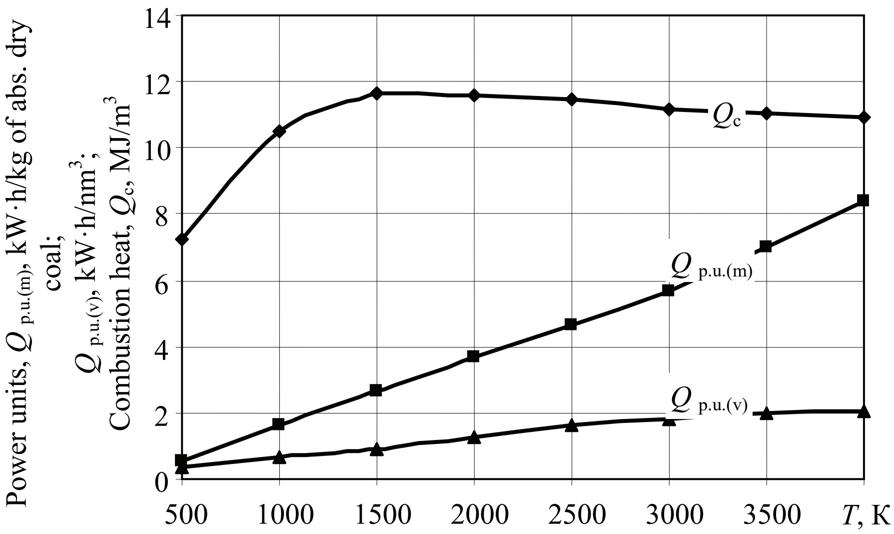

Figure 2. Indicators of the anthracite coal thermal transformation process.

Studies have shown that the maximum gas yield can be obtained by using an air oxidizing medium. But its energy component does not exceed 37 %, the remaining 60 % are neutral nitrogen from the oxidant (ballast waist gas). The calorific value of such gas does not exceed 4.6 MJ/m^3, which is two and a half times less than in an oxygen or steam oxidizing medium.

The minimum gas yield is obtained in an oxygen medium. The main components of the gas phase are CO and H_2. The yield of CO is 80 % of the total gas volume. The yield of H_2 is 14.19 % of the total gas volume. The energy components of the gas in an oxygen medium comprise 94 %, its calorific value reaches 11.5…12 MJ/m^3. The disadvantages of oxygen blast are the low total yield of the gas phase, unsatisfactory (value less than 1) indicator of the hydrogen oxide number (H_2/CO) and the high cost of special equipment for the production of oxidant.

Energy consumption of the conversion process, both mass ($Q_{p.u.(m)}$) and volumetric ($Q_{p.u.(v)}$), depending on the temperature is almost linear (figure 2). The mass energy consumption of transformations largely depends on the amount of carbon (C) in the conversion medium. The more carbon (C), the more oxidizer (O_2) is needed which energy consumption is high. In combined schemes, the oxidant generation process is combined with the processes of conversion and plasma formation, so the energy consumption is also combined. For steam blast, the energy consumption of the oxidant generation from water is associated with an increased total amount of gas and with the transition of H_2 to the gas phase. For this reason, the volumetric energy intensity, in contrast to the mass energy intensity, decreases with increasing C in the conversion medium (table 1).

Table 1. Comparison of the main indicators of the coal and sludge thermal transformations in different oxidizing media.

Oxidant	Medium C, %	Indicators of thermal transformations (T =1800 K)						
		The outlet of the gas phase, $V_{g.ph}$, nm^3	V_{CO}, m^3/kg	V_{H2}, m^3/kg	$V_{(H2+CO)}$, m^3/kg (%)	Specific mass energy consumption, ω^{μ}_{pu} , kWh/kg	Specific volumetric energy consumption, ω^{V}_{pu} , kWh/m^3	Q_c, MJ/m^3
steam	Anthracite	2.88	1.37	1.48	2.85 (99)	3.66	1.27	11.56
air	73.54	3.77	1.05	0.19	1.24 (33)	3.26	0.86	4.07
steam	Sludge	1.14	0.47	0.43	0.9 (79)	1.62	1.62	9.31
air	27.13	1.11	0.43	0.18	0.6 (54)	1.22	1.1	6.63

The lowest energy consumption is observed in air blast due to the extraction of oxygen from the air with low energy consumption. However, in this case, the caloric value of gas is almost 2 times lower due to the low content of the energy component (table 1). The energy efficiency of the process also largely depends on the quality and nature of the oxidizing medium. Research has established a general balance of energy conversion and its distribution in the medium of the conversion process, as well as in the obtained products of the process (table 2).

Table 2. The total energy balance of coal conversion and energy efficiency of the process in various oxidizing media.

Oxidizing media		steam	air
Consumable energy, kWh	Physical energy of coal, $Q_{ph.c}$	0.005	0.005
	Physical energy of oxidant, $Q_{ph.o}$	0.0003	0.256
	Coal combustion heat, Q_{c}.	7.97	7.97
	Energy consumption of the process, $Q_{e.p}$	3.66	3.26
	Energy obtained, ΣQ_{ob}	11.63	11.49
Received energy, kWh	Gas combustion heat release, $Q_{g.}$	9.24	4.53
	Gas energy, $Q_{g.e}$	2.1	2.03
	Ash energy, $Q_{a.e.}$	0.13	0.13
	Energy consumption, $\Sigma Q_{e.c.}$	11.47	6.69
Efficiency, η		0.986	0.58

It is obvious (table 2) that the energy spent on media conversion ($Q_{e.p.}$) by means of air is 11 % lower than the energy of steam plasma. However, the energy distribution in the transformation products is different. The energy value is 2.3 times higher in the steam gas phase. In the case of air oxidizer, more than 60 % of energy is concentrated in the gas phase. It should be taken into account when choosing the technology of further utilization of conversion energy as well as it should be noted that 55…69 % of energy is located in neutral nitrogen.

It is established that for steam medium utilization as an oxidizer, the gas phase yield is 35…40 % higher than in the oxygen blast due to hydrogen from the oxidizing medium. The energy efficiency value of the process is close enough 1 (steam blast) and does not exceed 0.8 when using oxygen utilization. For air blast despite the lowest energy consumption of transformations and high gas phase output, the energy efficiency barely reaches 0.6.

Energy consumption of the process can be reduced by regeneration of the energy for the obtained gases, the temperature range of which 1700…1750 K. Energy consumption increases the temperature of the initial components (coal and water). The dependence of the energy consumption on the initial temperature is shown in figure 3.

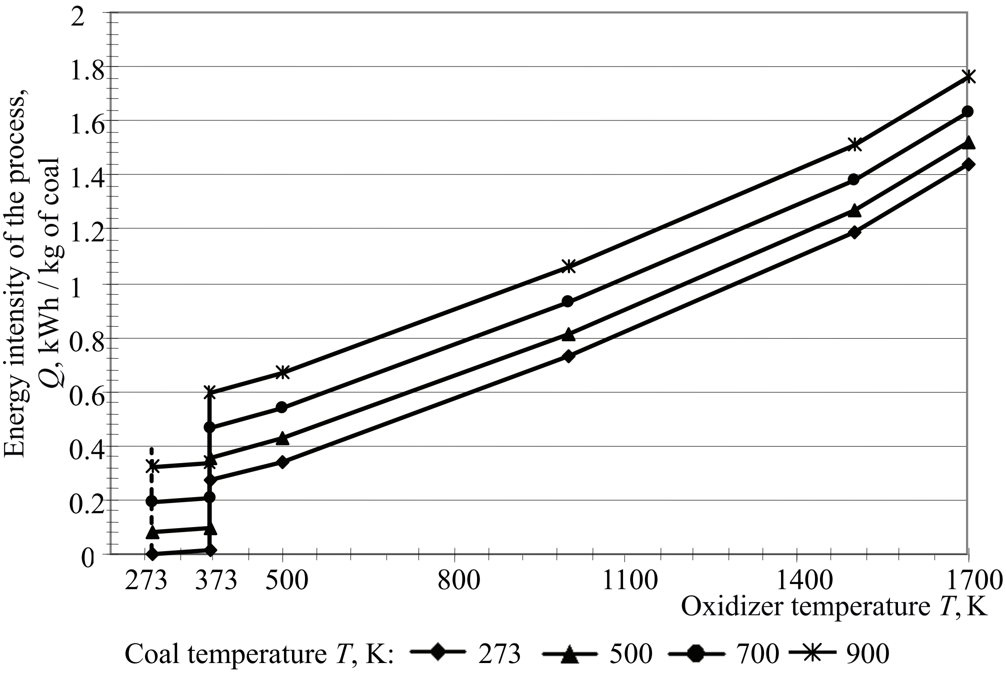

Figure 3. Dependence of energy consumption of coal-to-gas conversion on the initial temperature of the reacting components.

Every 100 K of the oxidizer and coal temperature increasing due to the utilization of exhaust gases heat leads to decreasing of the exhaust gases by 0.1...0.13 kWh. Thus, heating of the oxidizer up to 1700 K as well as coal heating up to 900 K lead to the increasing of the exhaust gases heat up to 88 %. For conditions of the heating of the reacting components to the temperature range of 700…800 K, 0.9 kWh of exhaust gas energy will be used, that can reduce the energy consumption of conversions by 25… 30 %. The remaining heat (about 1.1 kWh from obtained 1 kg of coal converted to gas) can be used for other purposes. Thus, by changing the degree of recovery factor of the exhaust gases heat value, it is possible to regulate the energy consumption of the conversion process and reduce the total cost of the process of coal conversation into gas.

The technological scheme of allottermic processes of coal conversion into gas that takes into consideration the influence of low-temperature plasma energy is presented in figure 4. It shows the sequence of transformation processes of homogeneous and heterogeneous organic media under the influence of plasma energy flow (split circuits) or under the influence of direct arc discharge (combined circuits). The ways of realization of the process both in the mode of gasification of the organic part of the raw material and its complex processing, including the mineral part are given.

Probable consumers of coal conversion products are presented in figure 4.

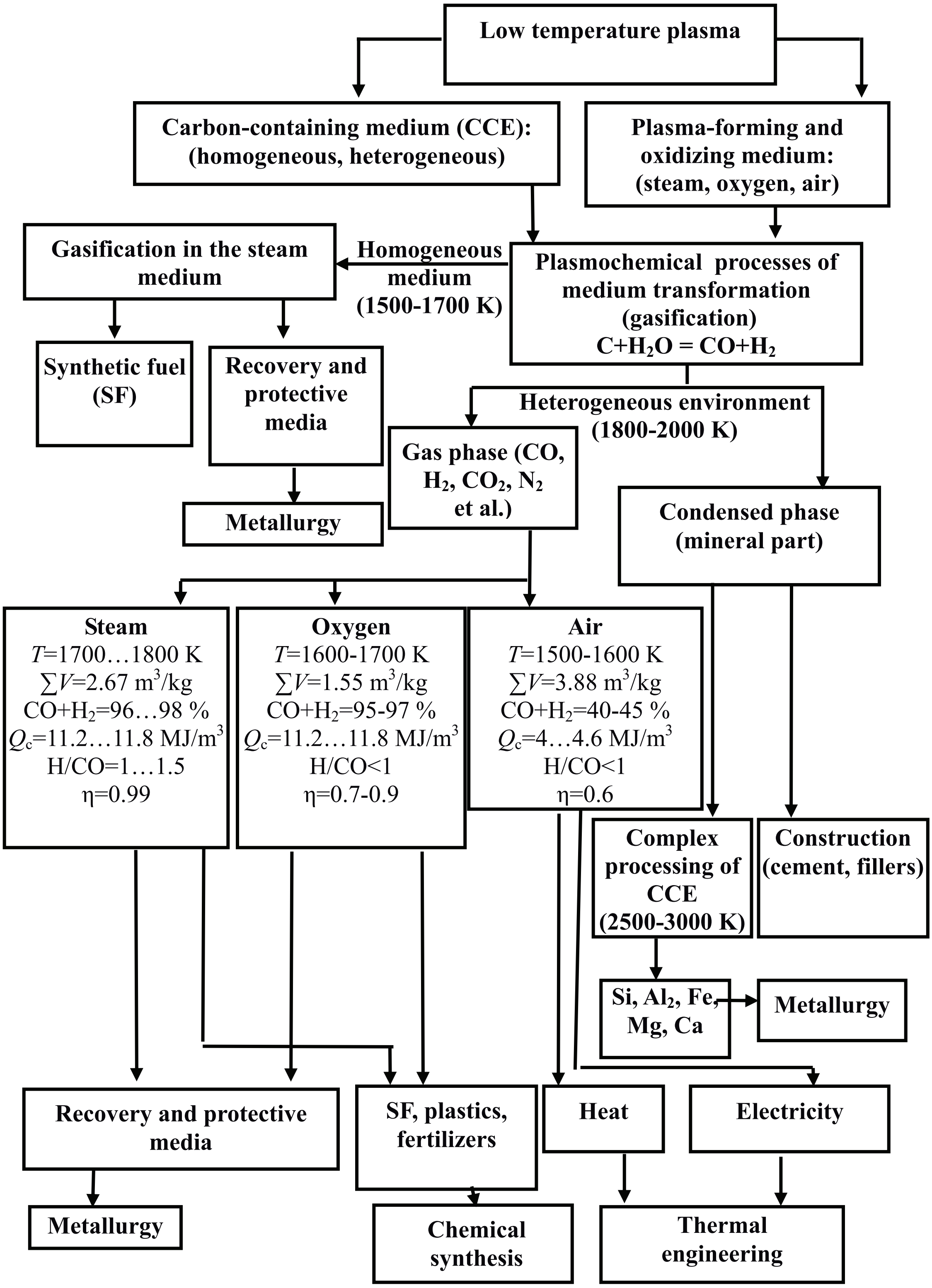

Figure 4. Technological scheme of carbon-containing media transformations by means of low-temperature plasma energy.

For the determination of the efficiency of steam-plasma gasification of coal, the dependences of the cost of synthetic motor fuel (SMF) production on the cost of raw materials and energy for conversions are established. The cost indicators of SMF production from natural gas by well-known companies Sasol, Syntroleum, BP (figure 5) and from coal by steam-plasma conversion into gas are compared. The zones of economic efficiency of SMF production by the considered technologies were established. The methodology of calculation and comparison of indicators is given in [13].

It is obvious (figure 5) that each of the considered technologies becomes effective when the price of crude oil exceeds 40...45 dollars/bar. Further price increasing raises up the efficiency of SMF production by any of the known technologies, including steam plasma technology. The price of SMF production depends on the cost of raw materials (coal, gas), electricity and technology. Thus, the growth of raw material prices sharply limits the economic efficiency zone of SMF production by autothermal technologies. This could be explained by the transition the part of the cost of raw materials used to convert it into gas to the cost of SMF. This can be seen from the angle of the lines inclination of the autothermal reactions (figure 5). Steam plasma technology is more significantly relies on the price of energy supplied from outside. Steam plasma technology remains competitive in the SMF market among the world's leading companies for the range of coal prices 30…45 USD/ton and electricity 0.7...1.3 UAH/kWh as well as oil price not lower than 45…50 USD/barrel. Steam plasma technology is less sensitive to this indicator, which improves the prospects for its realization.

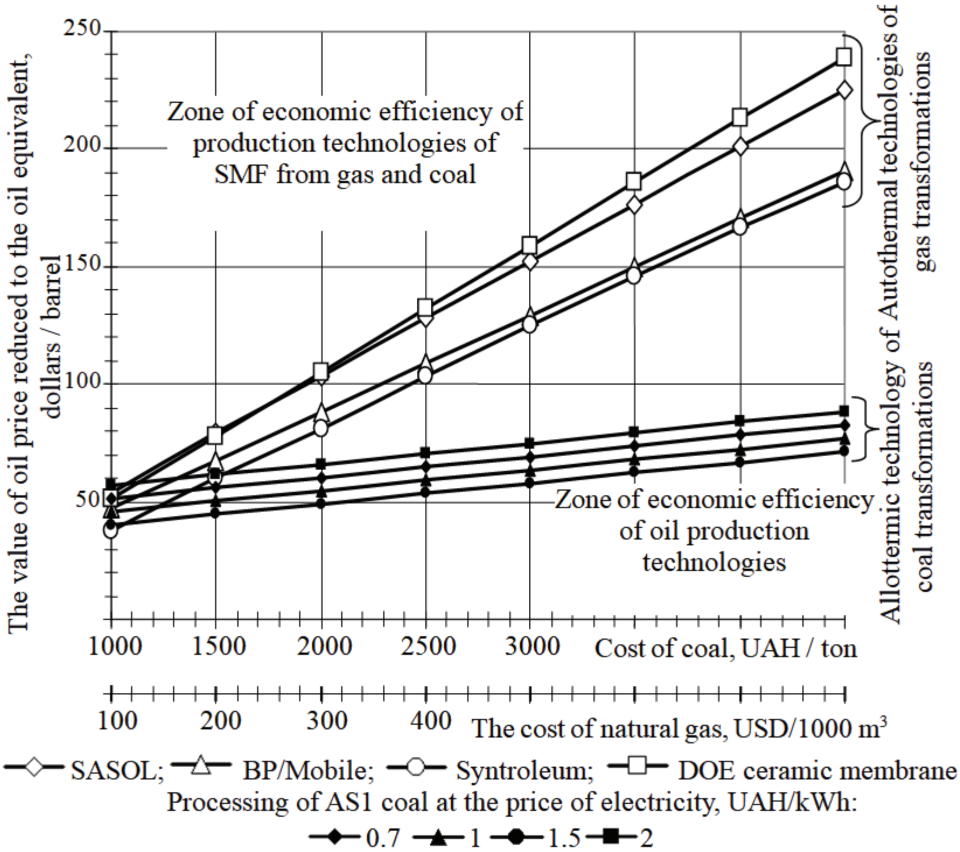

Figure 5. The cost of SMF, which is equivalent to the cost of oil, depending on the cost of raw materials and electricity.

The most significant advantage of steam-plasma conversion of coal into gas is a complete solution of environmental problems of common use of "dirty" energy sources as an alternative to oil and gas. Harmful and waste compounds of the gas phase (CO_2, NO, NO_2, SO) in steam-plasma processes do not exceed 1.0…2 mol/kg or 0.5…1.5 % of the total mass of gases. The temperature in the reaction space that exceeds 2000 K provides the destruction of any harmful and toxic compounds, including sulfur, reducing emissions to the level below European standards.

4. Conclusions

For allottermic processes of carbon-containing media conversion into gas the lowest energy consumption is observed in air blast. But these processes have a low efficiency. The highest efficiency is achieved when using a steam medium as an oxidant. In this case, the output of the gas phase is 35...40 % higher than with oxygen blast.

Thus, allottermic low-temperature plasma technologies stand out by the versatility of recycled raw materials, environmental safety, low metal consumption of equipment and capital costs. These technologies would become the basis for further development of technologies for thermal conversion of carbon-containing media (including municipal solid waste) into the special industrial products.

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