STUDY OF SEVERAL REACTOR CONSTRUCTION DESIGNS IN APPLICATION TO THE PROCESS OF OIL PYROLYSIS IN A PLASMA JET

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The possibility of plasma jet pyrolysis of oil in a direct flow reactor and a reactor with a reverse flow design was confirmed experimentally. A comparison was made of the technological output of gaseous products for different system parameters for both construction variants.

The problem of choosing the most rational design from those known at present for the mixing of a plasma jet with raw materials is examined in the present article. The two schemes most acceptable for the given process from our point of view were compared: direct flow (injection of raw material perpendicular to plasma jet), and counter flows whose constructive solution was obtained in reactors of an analogous type. Some deviation from normal practices was inherent to the reactor using the counter flow system, since it finally became a two-stage reactor in the first stage of which the plasma jet was mixed with the starting raw materials by the counter flow system, while the second stage had the form of a quenching apparatus in which quenching of the pyrolysis products by cold gas is combined with their cooling on the cold surfaces of a heat exchanger.

The pyrolysis of directly distilled oil in a low temperature plasma jet was chosen as the model process.

A plasmotron of the core type using nitrogen as the plasma-generating gas was used in both design variants. In the plasmotron power range from 10 to 22 kW and 60-90% efficiency the average plasma temperature varied in the interval of 3500-7000°K, which provided a range of average enthalpies of the reaction components obtained in the reactor mixing from $0.4 \cdot 10^3$ to $1.2 \cdot 10^3$ kcal/kg for the various systems. Here the average enthalpy of the mixture of plasma-generating gas and pyrolyzed raw materials in the reactor was calculated as the difference between the power supplied to the reactor by the plasma-generating gas and raw material and the power lost in cooling the construction components of the entire reactor in operation by the direct flow system or only in the first reactor stage in operation with the reverse flow system.

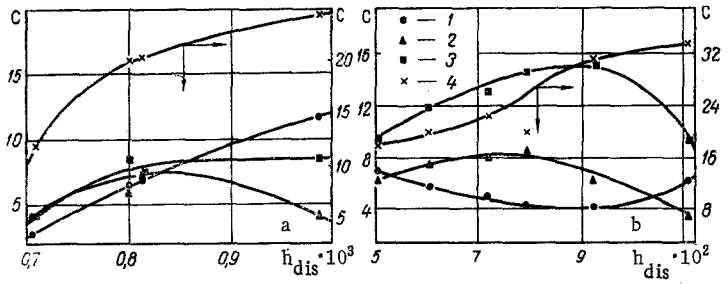

Fig. 1. Dependence of pyrolysis gas products yields C, %vol on enthalpy h_{dis}, kcal/kg for direct flow design (a) and with opposite streams (b): 1) C_2H_2; 2) $C_2 \cdot H_4$; 3) CH_4; 4) H_2.

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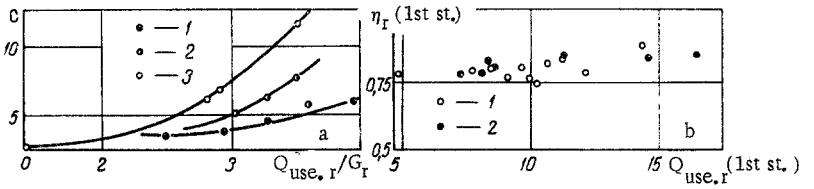

Fig. 2. Dependence of C_2H_2 yield on specific energy in direct flow reactor (a) at consumptions of original raw material: 1) G_r = 1.85 g/sec; 2) 1.75; 3) 1.5, and thermal efficiency (b) on useful power: 1) for reactor using direct flow design; 2) for first stage of reactor with opposite flow. C, %vol; $Q_{use.r}/G_r$, kW·h/Nm^3.

Directly distilled oil from the Romashkinskii deposit with the following characteristics was used as the starting product in the experiments: specific gravity 0.869 g/cm^3, viscosity 10.5 cP (start of bubbling 30°C); element composition (in %vol): C = 85.4, H_2 = 12.74, S = 1.61, $O_2 \approx 0.18$, and scale of bubbling:

°C	Up to 80	100	220	300
% vol	7,8	32,9	38,0	86,7

In all the experiments the raw material was injected into the plasma jet in liquid drop form through an atomizer from a feeder under a pressure of 6-10 atm. The flow rate of the raw material in the experiments was 1.5, 1.75, and 1.85 g/sec.

The pyrolysis gases at the output of the second (quenching) stage of the reactor were cooled in a tubular condenser, passed through a trap for liquid products, and entered a manifold for separating the gaseous products of pyrolysis for analysis and then were discarded into the atmosphere.

The gaseous pyrolysis products were analyzed by the method of gas absorption chromatography using two chromatographs, KhL-4 and LKhM-7a, on detector-catharometers.

In both chromatographs the adsorbent used was ASK silica gel modified with vaseline oil in a concentration of 10% of the weight of silica gel.

The components N_2 + HCN, CH_4, C_2H_6, C_2H_4, C_2H_2, and C_3H_8 were analyzed on the KhL-4 chromatograph using hydrogen as the carrier gas. Hydrogen in the pyrolysis gas was determined separately on the LKhM-7a chromatograph (Ar carrier gas). The experiment continued for 5-10 min. After reaching the stationary stage, determined by a chromel–alumel thermocouple, upon reaching a constant temperature at the output of the second reactor stage or after quenching in the direct flow design gas samples were taken for analysis in three to four pipettes uniformly during the time the experiment was conducted.

The dependence of the yields of gaseous pyrolysis products of oil in % vol on the enthalpy of the gases discharged from the reactor h_{dis} for the case of the direct flow reactor, and the enthalpy of the gases discharged from the first stage of the reactor h_{dis} (1st st.) for the counter flow design are presented in Fig. 1a and b. Among the curves presented in Fig. 1a and b the dependence of the yields of acetylene are most interesting, which in the case of the counter current has a minimum in the region of h_{dis} (1st st.) $\simeq$ 0.9 $\cdot 10^3$ kcal/kg, while for the direct flow with an increase in h_{dis} the acetylene content grows with the increase in enthalpy. As regards the ethylene yields, it is seen from Fig. 1 that the nature of the dependencies presented for both variants coincides with the maximum in the enthalpy region of 0.7-0.8 kcal/kg. The absolute yield of ethylene is higher for the counter flow and reaches a value of 8-9%vol.

In view of several differences in the geometrical sizes of the reactor construction designs compared, the comparison of the results of the pyrolysis process was carried out with the condition of maintaining approximately the same thermal reactor efficiencies for the characteristic operating conditions of the systems which were compared. In connection with this the dependence of the thermal efficiency of the reactor (or its first stage in the counter flow case) for both designs on the amount of heat $Q_{use.r}$ usefully employed in the reactor (or in the first stage, respectively) is presented in Fig. 2b.

The dependence of the yields of gaseous products on the specific energy consumption $Q_{use.r}/G_r$ is shown in Fig. 3, analogous to those shown in Fig. 1a, b.

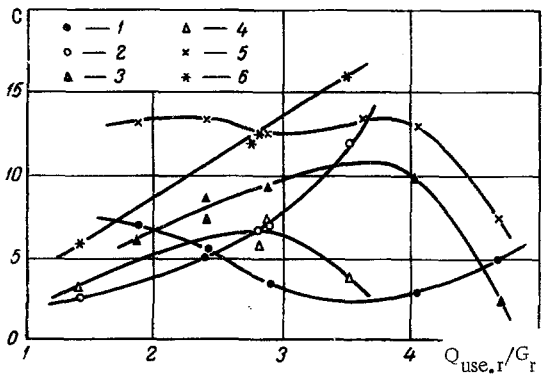

Fig. 3

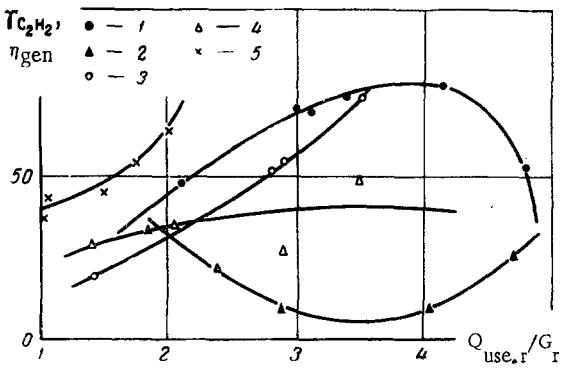

Fig. 4

Fig. 3. Dependence of yield of C_2H_4, C_2H_2, and $\Sigma(C_2H_2 + C_2H_4)$ on specific energy: 1) C_2H_2 (opp.); 2) C_2H_2 (dir.); 3) C_2H_4 (opp.); 4) C_2H_4 (dir.); 5) $\Sigma(C_2H_4 + C_2H_2)$ (opp.); 6) $\Sigma(C_2H_4 + C_2H_2)$ (dir.). C, %vol.; $Q_{use.r}/G_r$, kW·h/Nm^3.

Fig. 4. Comparison of dependencies of general degree of conversion η_{gen} (%) and conversion to acetylene $\gamma_{C_2H_2}$ (%) on the specific energy consumption in a direct flow reactor and in a reactor with opposite flow: 1) η_{gen} (opp.); 2) η_{gen} (dir.); 3) $\gamma_{C_2H_2}$ (opp.); 4) $\gamma_{C_2H_2}$ (dir.); 5) η_{gen} according to data of [1]. $Q_{use.r}/G_r$, kW·h/Nm^3.

The comparative dependencies presented in Fig. 3 for the sum of unsaturated hydrocarbons clearly favor the opposite flow, since in the wide range of values of $Q_{use.r}/G_r$ from 2 to 4 the sum $\Sigma C_2H_2 + C_2H_4$ maintains an almost constant value while for the direct flow it increases only with the increase in $Q_{use.r}/G_r$, exceeding the results for the opposite flow design only at values of $Q_{use.r}/G_r > 3.0$. Thus, it is evident that in using a reactor with the opposite flow design it is possible to obtain about the same yield of total C_2H_2 and C_2H_4 at low energy consumption. An analysis of the acetylene yield as a function of the specific energy consumption $Q_{use.r}/G_r$ for the direct flow design at different flow rates of the original raw material is presented in Fig. 2a. Reducing the consumption of raw material G_r from 1.85 to 1.5 g/sec with a simultaneous increase in $Q_{use.r}/G_r$ leads to an increase in the acetylene yield (to 12 %vol) which is fully explained by the presence of a larger enthalpy potential of the mixture in the reactor due to the lower consumption of the raw material supplied. The presence of extremal dependencies of the C_2H_2 yield in the reactor having opposite flow can be hypothetically explained by the quenching conditions, which were taken as identical for both variants but were optimal for the direct flow. In connection with this the construction design of the cooling stage for the reactor with opposite flow evidently requires final development and a further detailed study.

The general degree of conversion η_{gen} and the degree of conversion to C_2H_2, $\gamma_{C_2H_2}$, as functions of the specific energy consumptions $Q_{use.r}/G_r$ is shown in Fig. 4. Some increase is evident in η_{gen} (by about 10%) for the system with opposite flow, which is most noticeable in the region of values of $Q_{use.r}/G_r < 3.0$ kW·h/Nm^3. However the presence of an extremal dependence for C_2H_2 once again causes one to examine the still unstudied region of values of $Q_{use.r}/G_r$ = 1.0-2.0, since in the region studied a decrease in the specific energy consumption from 3.0 to 2.0 kW·h/Nm^3 leads to an increase in C_2H_2 yields and in the respective degree of conversion $\gamma_{C_2H_2}$.

The dependence of η_{gen} on $Q_{use.r}/G_r$ according to literature data [1] for pyrolysis of low octane benzene in an argon plasma jet is also presented for comparison in Fig. 4. Evaluation of the increase in specific energy consumptions during pyrolysis of oil should be performed with regard to the fact that in the present work the oil was injected in liquid drop form, while in [1] a vapor form was used.

The problem was not raised in the article of achieving the maximum yields of acetylene (or the sum of acetylene and ethylene) as indicated by the choice of plasma-generating gas, although the results obtained on the yield of acetylene up to 12%vol and of ethylene to 8-10% vol are sufficiently high even in comparison with the pyrolysis of oil in a hydrogen plasma [2], where an acetylene concentration on the order of 15% was obtained. One should also note the absence from the results of the analysis of unsaturated hydrocarbons with C > 3 (in some experiments ethane and propane were also obtained in concentrations not exceeding 1.0%vol) which may have a definite advantage in some cases.

LITERATURE CITED

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