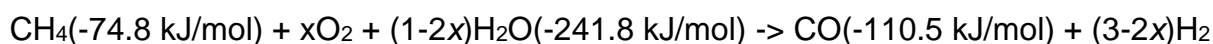


ENHANCING EFFICIENCY OF HYDROCARBONS TO SYNGAS CONVERSION VIA PARTIAL OXIDATION

S.O. Dorofeenko, E.V. Polianczyk

*Institute of Problems of Chemical Physics RAS,
1 Academician Semenov ave., Chernogolovka, 142432 Russia; polian@icp.ac.ru*

The conversion of hydrocarbons to syngas should provide a maximum yield of carbon monoxide and hydrogen with the lowest attainable energy expenditure. In case of the partial oxidation conversion, the ideal process would be the one with zero net heat effect of gross reaction $\Delta H = 0$. Thus, additionally to oxygen it must involve an endothermic oxidant, e.g. water, to compensate the heat release of oxygen reaction. For methane the oxygen/methane ratio corresponding to zero heat effect is $x^* = 0.426$:



On the other hand, the conversion should be performed at a high temperature, otherwise the chemical equilibria will bring the reaction to methane, water, and carbon dioxide. The high-temperature reaction products carry away the reaction heat, which unavoidably is positive. A higher heat efficiency process can be achieved by recovery of the sensible heat of hot products to be transferred to raw reactants. That is superadiabatic combustion (SAC).

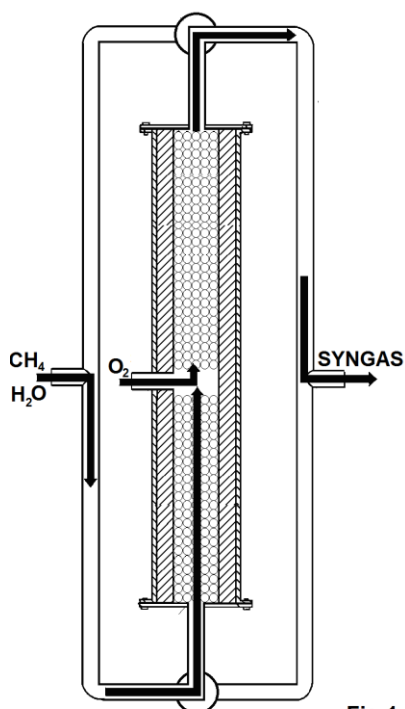


Fig.1

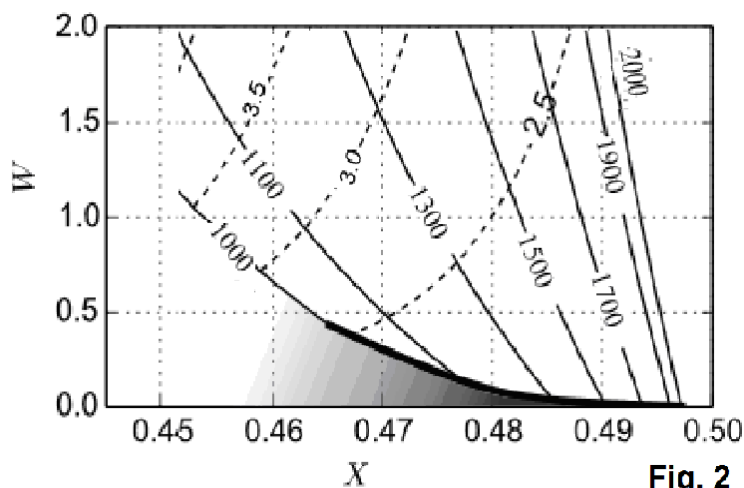


Fig. 2

The filtration combustion (FC) in a porous medium provides an opportunity to realize SAC, as the porous medium provides both heat exchange surface and a heat carrier. The traveling wave SAC of ultra rich gas mixtures was proposed [1]. However, the FC of premixed gases involves a fundamental limitation. A gas mixture ‘chooses’ itself a combustion temperature controlled by its own kinetics of ignition [2].

An improvement proposed by authors was to arrange non-premixed FC to provide preheating of one gaseous reactant from the porous medium prior to mixing and it can be arranged in reversed-flow reactor [3] (Fig.1) or a continuous flow reactor [4]. With steam-oxygen conversion this process with steam-methane preheating and pure oxygen supply (Fig. 1) promised as low x as 0.48 (Fig. 2).

Further improvement in the efficiency of conversion even with air used as an oxidant can be attained with preheating of both reactants [4, 5] (Figs. 3-4) in a moving bed reactor. Preheating of methane and partial preheating of air-steam mixture with residual heat of the solid heat carrier provide conversion with > 90% chemical efficiency for $x < 0.55$.

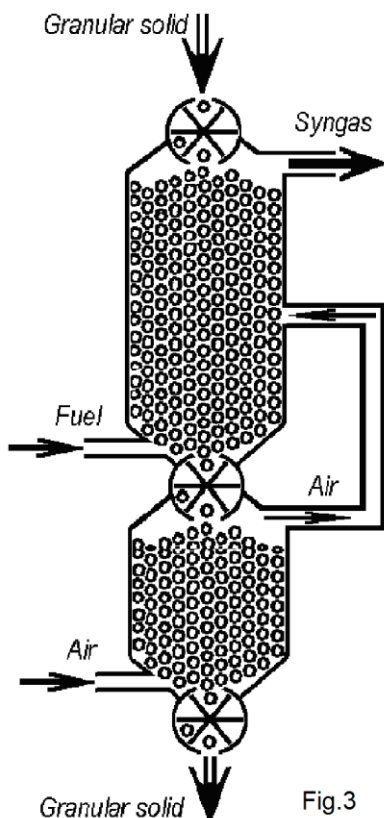


Fig.3

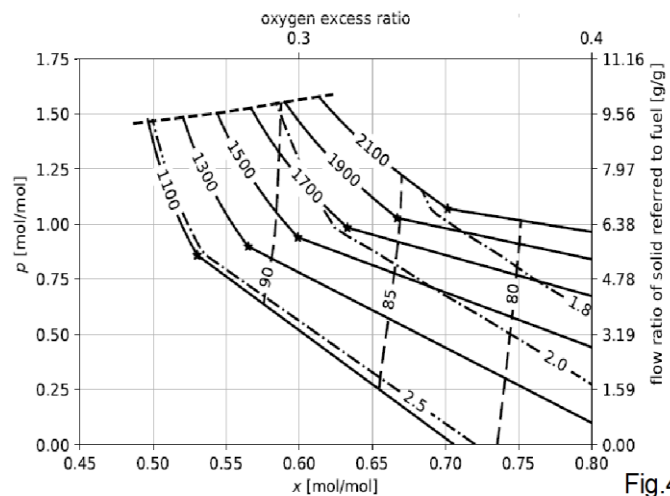


Fig.4

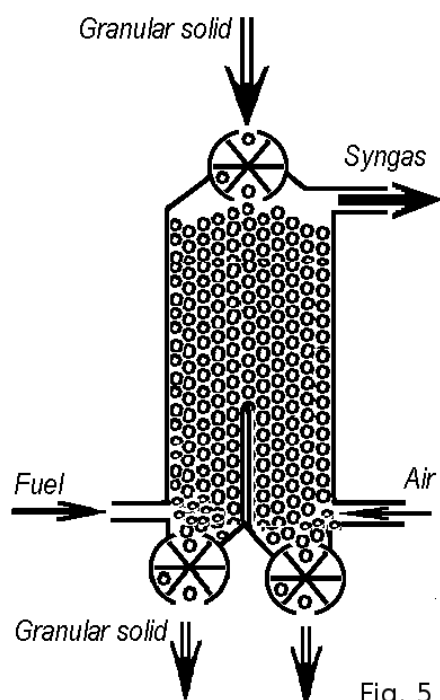


Fig. 5

The process in Fig. 3 provides very high efficiency even for low caloric pyrolysis gas [5]. Noteworthy is that the optimum heat recovery is attained for the flow of the solid heat carrier having heat capacity higher than that of the reactant gas yet lower than the flow of syngas.

Note also that in case of POX conversion the heat capacity of the reaction products (hydrogen and carbon monoxide) is higher than that of initial reactants (methane, oxygen, and water).

This consideration prompts a way for further improvement in the POX conversion. One should achieve a **complete preheating of both reactants**. Such reactor of a dream is schematically shown in Fig. 5. Looks not excessively feasible in its design, yet very promising in energy efficiency.

In the arrangement shown in Fig. 5, one can adjust the flow of the solid heat carrier to have the heat capacity higher than that of both reactant gases yet lower than that of the flow of syngas. Therefore, the conversion at with near ideal heat recovery becomes possible. With a perfect heat insulation both reactants are preheated to the reaction temperature prior to mixing and the syngas lends its sensible heat to the solid heat carrier to heat it to the reaction temperature. The condition of zero enthalpy of reaction $\Delta H = 0$ is **met at the reaction temperature**.

References

- [1] M.K.Drayton, A.V. Saveliev, L.A.Kennedy, A.A.Fridman, Y.-E.D.Li, Syngas production using superadiabatic combustion of ultra-rich methane air mixtures, Symp. (Int.) Combust. 27 (1) (1998) 1361–1367. doi:10.1016/S0082-0784(98)80541-9.
- [2] S.S.Kostenko, E.V.Polianchik, A.A.Karnaukh, A.N.Ivanova, G.B.Manelis, Khim. Fiz, (2006) 25 53-63 (in Russian)
- [3] S.Dorofeenko, E.Polianczyk, Conversion of hydrocarbon gases to synthesis gas in a reversed-flow filtration combustion reactor, Chem. Eng. J. (2016) 292,183–189. doi:10.1016/j.cej.2016.02.013.
- [4] S.O.Dorofeenko, E.V.Polianczyk, Enhancing efficiency of hydrocarbons to synthesis gas conversion in a counterflow moving bed filtration combustion reactor, Int. J. Hydrogen Energy (2019) Vol. 44, PP. 30039-30052. doi:10.1016/j.ijhydene.2019.09.208
- [5] Dorofeenko S., Polianczyk E. Russian Journal of Chemical physics (in press).

Acknowledgements

The study was partial financial supported by the Russian Foundation for Basic Research and TUBITAK within the framework of scientific project No. 21-51-46007.

This work was performed in accordance with the contract with the Russian Ministry of Science and High Education; state registration no. AAAA-A19-119022690098-3 (0089-2019-0018).