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HYDROGEN PRODUCTION FROM BIOGAS

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There are many methods for hydrogen production from methane depicted in the literature. Among them are steam and steam-oxygen reforming, partial oxidation, and autothermal reforming, that is a combination of the two aforesaid technologies in one apparatus. Carbon dioxide reforming is also worth mentioning.

The following global reaction mechanisms are usually assumed for these technologies:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

$$CH_4 + 1/2\,O_2 \rightarrow CO + 2H_2$$

$$CH_4 + CO_2 \rightarrow 2\,CO + 2H_2$$

The first and third global reactions represent industrial processes that occur on metal or oxide catalysts, whereas the second reaction can be conducted both catalytically and as a homogeneous reaction. It is the latter variant which is widely realized on a commercial scale. Biogas is normally a complex mixture containing, along with methane, nitrogen and carbon dioxide that are not virtually oxidized in the course of partial oxidation process. According to the literature data CO_2 content in biogas can amount to 20 or 50%. Therefore feasibility of hydrogen producing from biogas is heavily dependent on how the presence of large amounts of carbon dioxide would affect the efficiency of various methane reforming processes.

As follows from general consideration, the efficiency of the most popular steam reforming process on nickel catalysts at high temperatures would be fairly low because the catalysts would be rapidly deactivated. Carbon dioxide is an obvious component participating in a carbon dioxide reforming process where the CH_4/CO_2 ratio is kept close to 1, however this ratio in biogas varies in a large range.

As to homogeneous partial oxidation with oxygen in various combustion regimes, we failed to find literature data which would allow us to infer whether carbon dioxide is a completely inert species or an active participant in the partial oxidation process. It is quite obvious that the end products, such as CO, hydrogen, and water do not virtually react with CO_2 under the conditions inherent in the homogeneous process. However it is not the case with reactive intermediate products, such as hydrogen atoms and various radicals present in the flame in superequilibrium amounts. We would like also mention carbon molecules C_2 and C_3, that are detected in flames as intense sources of luminosity (Swan bands in the visible range). In this connection contribution of the following reactions

$$C_2 + 2\ CO_2 \rightarrow 4\ CO \text{ and}$$

$$H + CO_2 \rightarrow CO + OH$$

must be evaluated. Reactions involving CO_2 and fractal soot predecessors that contain weakly bonded hydrogen are also to be considered.

The paper presents data on the composition of the end products formed after combustion of various hydrocarbon mixtures imitating biogas in both flame and self-ignition regimes. The effect of the presence of higher hydrocarbons in the mixture is also ascertained. Tests with various concentrations of higher hydrocarbons in methane at a constant equivalence ratio value reveal an interesting fact, namely, the CO/CO_2 ratio in the products increases as the number of C atoms increases in original stock. The possible reason of this observation is discussed.