



Direct Oxidation of Waste Hydrocarbon Gases to Oxygenates as a Perspective Tool for Decreasing of Atmospheric Pollution

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Abstract

Global warming is one of the most difficult problems of this century. We argue that it is unreal to prevent future climate change by collecting enormous antropogenic emission of carbon dioxide. More reasonable may be the collecting and processing much lower and more valuable emissions of other greenhouse gases, first of all methane. But industry needs new low-scale technologies to accomplish this task. Direct oxidation of hydrocarbons to liquid oxygenates may be the real solution.

Global warming arouses deep anxiety of world community. It is accepted to consider that the main reason of observed climatic changes is the antropogenic pollution of atmosphere by greenhouse gases. Though this opinion is questionable enough [1], the world community and political elite, alarmed by the future of mankind, insist on acceptance of emergency measures to reduce the emission of greenhouse gases. The most prominent and well-known measure in this area is Kyoto Protocol on climate change of 1997. According to the Protocol the leading industrial powers had to reduce by 2008-2012 years their emission of greenhouse gases on the average to five percent as contrasted to by the level of 1990.

The policy of Kyoto Protocol is directed first of all on the reduction of the emission of main greenhouse gas – carbon dioxide. Really, carbon dioxide gives the largest contribution to a greenhouse effect [2] (Fig. 1). However, it does not eliminate considerable influencing of the remaining factors. The climate forcing (change of a flow of solar radiation reaching earth surface induced by a certain factor) for the last 150 years of the second on value greenhouse gas - methane - makes the half of that of carbon dioxide. It is in spite of the fact that its emission and concentration in atmosphere is lower more than two orders of mag-

nitude. The climate forcing of freons, tropospheric ozone and nitrous oxide also is appreciable enough. And climate forcing of tropospheric aerosols and change, caused by them in a cloudy coverage, are practically equal to climate forcing of carbon dioxide, but have the opposite sign.

Certainly, any reduction of carbon dioxide emission, reasonable from economic point of view, had to be welcomed. For example, the USA has reduced the specific emission of CO₂ per 1 million dollars of Gross Domestic Product (GDP) from 330 t in 1980 to less than 240 t in 1998 [3]. The significant contribution to global reduction of CO₂ emission can provide modern technologies in power generation. The introduction of modern combustion turbines and preliminary gasification of solid fuel and high-gravity residuals of oil processing may raise efficiency of fuel usage from 32 percent for standard electricity generating plants up to approximately 49 percent [4].

But attempts to collect and process any significant part of approximately 20 billion t/year of antropogenic emission of carbon dioxide appear as unreal. Almost 90 percent of antropogenic emission of CO₂ are outlet gases of power generating plants, where CO₂ concentration is only 12 percent. It means, that it is necessary to process the essential part from almost 200 trillion cubic meters of annual emission of world

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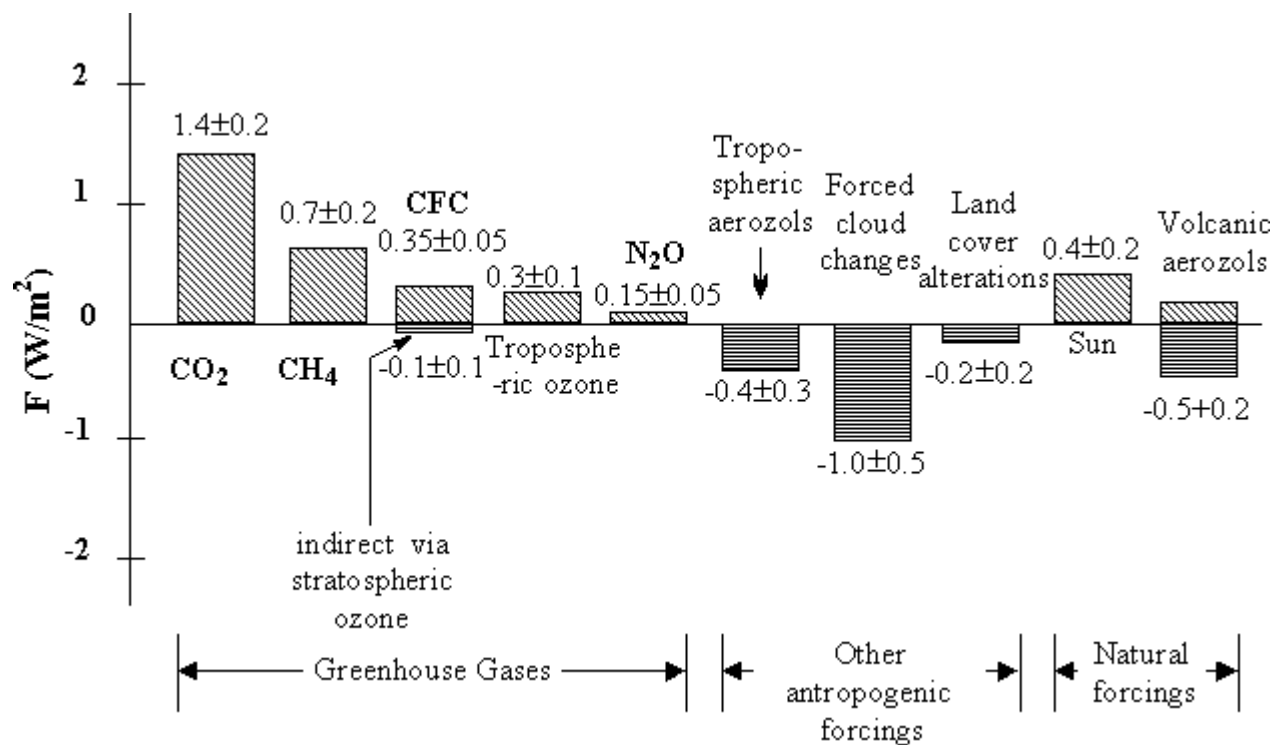


Fig. 1. Climate forcings F (W/m²) of different atmospheric factors from 1850 for 2000 [2].

power engineering. The cost of CO₂ collecting now amounts from 100 up to 300 dollars per ton [5], that considerably exceeds the cost of oil or gas (and each ton of the burned hydrocarbon fuel results in formation about three tons of carbon dioxide). Even if it will be possible to reach considerably lower costs, what looks very unlikely, the spending will be all the same huge. Besides, the carbon dioxide is produced mainly in the same processes of power generation, in which the main part of anthropogenic aerosols with opposite climate forcing emerges. So the general climate effect of these two factors is very close to zero.

Therefore, it seems that the more effective will be the elaboration of measures for collecting and processing significantly smaller on volume greenhouse gases with much larger climate forcing: nitrous oxide, tropospheric ozone, soot etc. Especially it concerns methane, which has independent power value. Its collecting and processing in many cases may be economically profitable. Probably, it is more reasonable to concentrate the main efforts of the world community just on this direction in attempt to prevent future undesirable climate change [1].

Though the main anthropogenic source of methane is not the industry but agriculture, where its collecting is considerably more difficult, the fraction of the power generation in methane emission is also high enough

and reaches almost 30 percent (Table 1). At present processes of oil and gas production, transportation and processing, up to 4 percent of a world hydrocarbon gases production is vented in atmosphere or flared [6] (Fig. 2). In most cases, power industry vents and flares gases with high content of homologues of methane [7] (Table 2), i.e. most valuable hydrocarbon stuff. However, huge quantity of small-sized sources of these gases dispersed on the vast regions of oil and gas production, makes their collecting and processing at present technologies unprofitable. It is necessary to evaluate principally new low-scale processes that will make it possible to convert these hydrocarbon gases into more easily transportable liquid products [8].

Now in connection with a recent sharp and, probably, irreversible increase of the oil prices there is a considerable interest to conversion of natural gas in liquid products (Gas to Liquids, GTL). All the most prominent world corporations in this area have designated their interest to such technologies [9] (Table 3). However, in all cases it considers the possibility of construction of large-scale plants with specific investments in the range of 25-40 thousand dollars per barrel of daily production. If we take into account the significant increase of specific capital investments with decrease of plant capacity, the real investments

Table 1
Anthropogenic sources of methane emission.

Source	Share (%)
Domestic wastes	7
Combustion of biomass	11
Garbage dumps	10
Oil	4
Coal	12
Natural Gas	11
Rice fields	16
Domestic animals	29

in low-scale installation with annual production on a level of 25 thousand t of liquid products will be about 30 millions dollars, that is economically unacceptable. The principally new technologies in this area are needed.

Real perspective to become the basis for creation

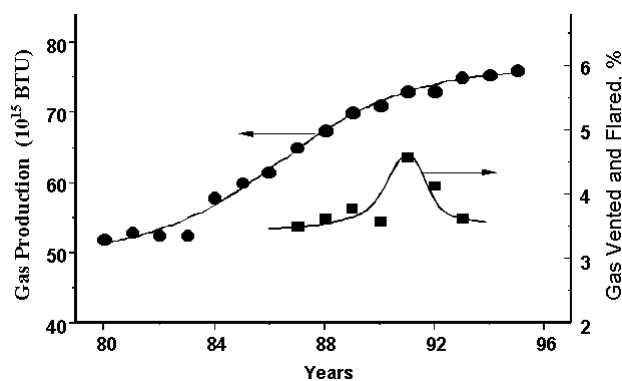


Fig. 2. World Dry Natural Gas Production (●) and Percent of Gas Wasted and Flared (■) [6].

of such low-scale technologies has the process of direct oxidation of hydrocarbon gases to oxygenates. The foundations of the theory of this process were elaborated [10], and now the technology is under development. Main products of direct oxidation of dry methane gas are a methanol and formaldehyde. The advantages of the process are well known. It is a capability to produce valuable products directly in the first stage, exothermicity, i.e. absence of additional

Table 2
Averaged composition of flaring gas condensate [7]

Component structure, % of weights.	Deposits	
	Sulfurless	Sulfur-bearing
Methane CH ₄	5,84	17,9
Etane C ₂ H ₆	6,64	2,5
Propane C ₃ H ₈	11,64	2,4
Butane <i>i</i> -C ₄ H ₁₀	9,56	0,7
<i>n</i> -C ₄ H ₁₀	5,31	2,1
Pentanes <i>i</i> -C ₅ H ₁₂	5,35	-
Hexanes C ₆ H ₁₄	47,76	-
Higher hydrocarbons C ₅₊	-	24,3
Carbon dioxide CO ₂	-	10,1
Nitrogen N ₂	-	0,1
Hydrogen sulphide H ₂ S	-	39,0
Mercaptan sulphur RSH	-	0,8
Oxysulfide of carbon COS	-	0,1
Density ρ , kg/m ³	2,82	1,1365
Heat of combustion, lowest Q_H , kcal/m ³	25 286	13 963

The notice: the delete means absence of the data.

Table 3
Economic analysis (short-term case) [9]

Description	Exxon Mobil	Shell	Sasol	Syntroleum	Rentech	Intevap
Total installed cost (TIC), \$ million	-	-	395	455	468	373
Gross revenue, \$ million	-	-	86.2	77.5	97.8	94.1
Projected internal rate of return (IRR), %	12.9	12.5	14.5	11.2	13.9	16.6
Net present value, \$ million	85	75	108	33	110	156
Total liquid yield, b/d	-	-	15.300	12.000	16.450	15.300
TIC in \$/bbl	29.000	30.000	25.800	37.920	28.450	24.380

energy consumption and relative simplicity of the equipment, which let to create simple low-scale installations. The main lacks of the process are rather low selectivity (about 50 percent at oxidation of dry methane gas) and degree of conversion for one pass through the reactor (up to 5 percent), that makes it necessary to recycle a reaction mixture or use the cascade arrangement of several reactors. The reason in that the main component of dry natural gas - methane - is a relatively stable compound, more stable, than all desired products of its processing. Nevertheless, economical estimations demonstrate, that even

low-scale installations with capacity about 10 thousand t/year and cost about 3-6 millions dollars are capable to provide the cost price of methanol in the range of 60-70 dollars/t, that almost twice below the cost of methanol on standard high-scale plants. In Fig. 3 the flowchart of power generation-chemical process of direct oxidation of natural gas to methanol with cascade arrangement of reactors and recycling of reaction gas mixture is shown [8]. Depending on available infrastructure, gas composition and received products, needs in produced power etc. the different versions of the process are possible.

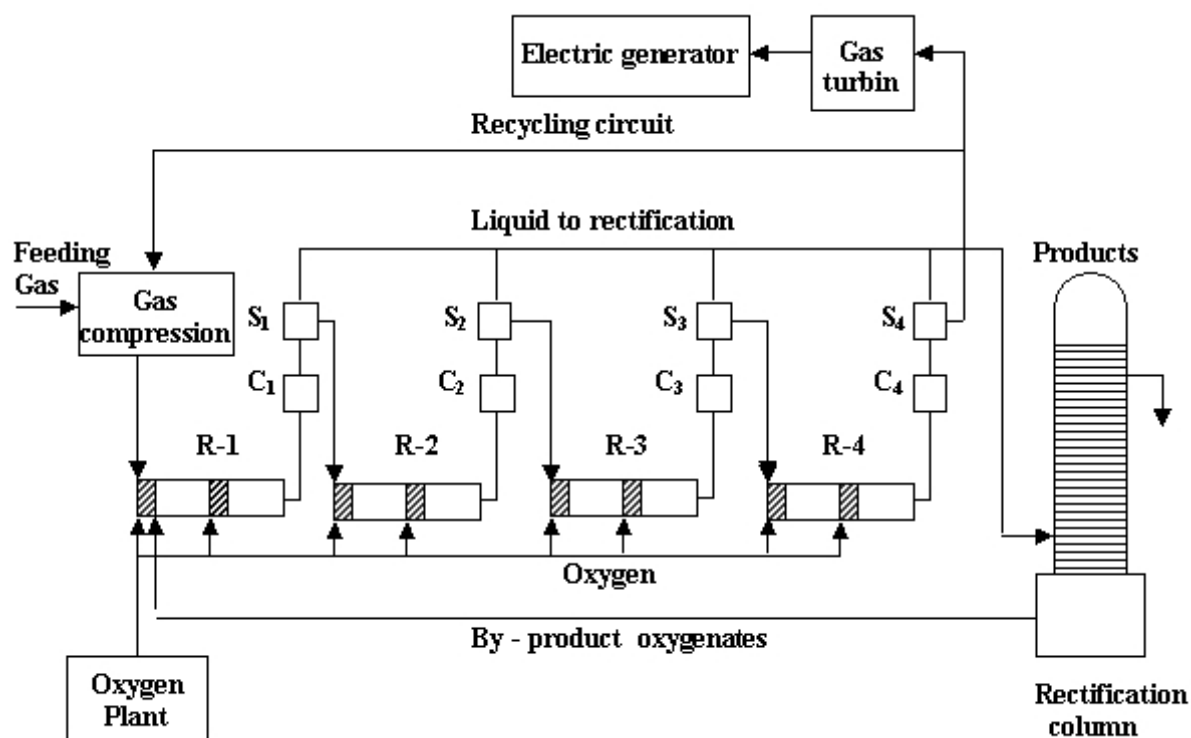


Fig. 3. The flowchart of power generation-chemical process of direct oxidation of natural gas to methanol with cascade arrangement of reactors and recycling of reaction gas mixture [8]. R - tubular reactors; C - coolers; S - separators.

But wasted in atmosphere or flared hydrocarbon gases, as a rule, contain considerable amount of C₂+ hydrocarbons (Table 2). And for such gases the outlook for this technology is considerably more favorable. Even small admixtures of higher hydrocarbons, at a level 5-10 percent, lower an operating pressure and temperature, increase selectivity of oxygenates formation and degree of gas conversion. At oxidation of C₂+ hydrocarbons, apart from methanol and formaldehyde, a number of other valuable products including ethanol and higher alcohols, *iso*- alcohols, higher aldehydes etc. are produced [10].

The design of profitable low-scale processes of direct oxidation of hydrocarbon gases to oxygenates would allow to resolve the problem of decreasing the air pollution by greenhouse gases and reduction of losses of hydrocarbon gases. But it also would allow resolving the problem of exploitation of low-deposit natural gases reserves and transportation of their power and petrochemical potential to places of potential consumption. From approximately 4,5 thousand main world gas fields only 2 percent that represent the most large-scale fields can serve as a feedstock for modern large-scale chemical processes [11]. The remaining 98 percent of fields can feed only lower-scale installations. And the most small-sized of them, probably, can not be at all involved in operation and maintenance phase without elaborating new low-scale processes of conversion of hydrocarbon gases in any liquid easily transportable products. It makes low-scale chemistry of natural gas one of the most perspective directions for the solution of ecological and power problems of 21st century.

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Received 03 May 2001.