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QUESTION OF CHEMICAL TRANSFORMATION OF UGC GASES

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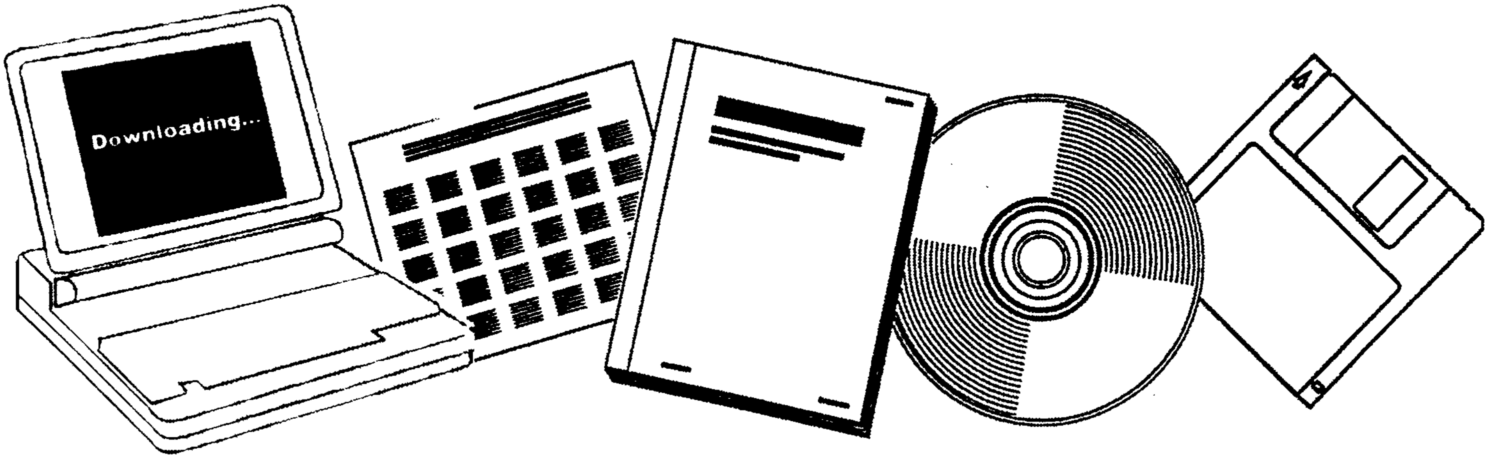

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ON THE QUESTION OF CHEMICAL TRANSFORMATION OF UGC GASES

– *as translated from* RUSSIAN

К ВОПРОСУ О ХИМИЧЕСКОЙ ПЕРЕРАБОТКЕ ГАЗОВ П.Г.У.

AUTHOR/S/ : I.F. BOGDANOV, V.Z. VOLKOV, A.M. MOSIN
AND I.L. FARBEROV

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LAWRENCE LIVERMORE LABORATORY
Post Office Box 808
Livermore, CA 94550

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ADDIS TRANSLATIONS INTERNATIONAL
3220 alpine road
portola valley, california 94025
(415) 854-6732

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ON THE QUESTION OF CHEMICAL TRANSFORMATION OF UGC GASES

I.F. BOGDANOV, V.Z. VOLKOV, A.M. MOSIN AND I.L. FARBEROV

As a raw material for chemical transformation, UGC gas has considerable shortcomings: a low content of potential hydrogen, high content of inert gases (CO_2 and N_2), presence of only 1-2% of methane, and several others. However, apart from this, the UGC* gas has some favorable features, which can be utilized only with a complex scheme of chemical transformation.

As is well known, UGC gas obtained with an air blast contains a high proportion of nitrogen. One of the methods of using up this nitrogen is the synthesis of ammonia, a problem whose desirability has been discussed in detail in [1] and with which we shall not be concerned here. It is also desirable to utilize the carbon dioxide, which could be the starting point for the synthesis of carbamide (urea), a product

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* Translator's note: Underground gasification of coal.

highly valuable for the national economy. The production of urea consists in reacting together NH_3 and CO_2, distillation of the synthesis products, and processing of the urea solutions into the finished product. There are various schemes for the production of urea, differing from one another by the apparatus, the methods of processing of the urea solutions, methods of utilizing the distillation gases, etc. [2].

The synthesis of urea from ammonia and carbon dioxide takes place in two stages. In the first of these the reactants are combined directly to form ammonium carbamate:

$$2NH_3 + CO_2 \rightleftarrows NH_2COONH_4 + 38.0 \text{ kcal}$$

In the second stage the carbamate splits off water and transforms into urea:

$$NH_2COONH_4 \rightleftarrows NH_2CONH_2 + H_2O - 6{,}8 \text{ kcal}$$

The process takes place with the formation of two phases: gaseous (NH_3, CO_2, H_2O) and liquid, consisted of molten ammonium carbamate, urea, and ammonium carbonates. In practice, the urea synthesis is carried out at 185-200°C. A higher temperature has an adverse effect on the apparatus, since corrosion is considerably increased.

Another, and no less valuable, product with major applications in the natural economy is methanol or methyl alcohol, which, like urea, can be obtained from UGC gases.

Methanol is made from carbon monoxide and hydrogen, according to the scheme:

$$CO + 2H_2 \rightleftarrows CH_3OH.$$

The above equation shows that in the formation of methanol one volume of carbon monoxide reacts with two volumes of hydrogen. This 1:2 ratio is precisely the ratio of the two gases in the UGC gas.

The position of equilibrium during methanol synthesis depends on the temperature and pressure. Therefore, as in the ammonia synthesis, to obtain considerable yields of methanol it is necessary to use a fairly high pressure. Thus, at 350°C and 100 or 300 atm the equilibrium contents of methanol during the passage of a $2H_2 + CO$ mixture are respectively 3.7 and 19.5%. It follows that methanol synthesis should be conducted at the highest possible constant pressure, which is a strong hindrance to the performance of this synthesis on the basis of UGC gas. However, in recent times I.A. Makarov and V.M. Nizyaev published a paper [3] showing that methanol synthesis can be conducted on a gas with a low proportion of CO, contrary to the earlier opinion that the synthesis must be done with pure gases. We consider it desirable to recommend performance of the methanol synthesis from UGC gases without their preliminary separation, but for this laboratory tests are required to see if the process can be carried out at a lower pressure, for example 100 atm. For this purpose a more active catalyst must be found.

Another method of industrial utilization of a mixture of carbon monoxide and hydrogen for the synthesis of organic compounds, in particular straight-chain hydrocarbons, is the Fischer-Tropsch process, which takes place according to the equation: $3CO + 3H_2 \rightarrow 2(CH_2<) + H_2O + CO_2$.

Here the ratio of the CO to the H_2 for synthesis is 1:1, though in practice use is made of gas containing slightly more hydrogen.

In the synthesis 1 m^3 of gas yields per pass 180-200 cm^3 of liquid hydrocarbons (benzine-oil), 10-15 g of high-molecular paraffin, and "gasol" (a mixture of gaseous hydrocarbons). By using cobalt catalysts and pressures of 5-15 atm it is possible to obtain from 1 m^3 of gas up to 80 g of solid paraffin apart from the benzine and oil. The product of synthesis with an iron catalyst contains many unsaturated and oxygen compounds, which may be processed into surface-active substances used in borehole drilling etc.

The Fischer-Tropsch synthesis can proceed with a CO/H_2 mixture diluted to 50% with inert gases, e.g. nitrogen, and this makes it possible to use for the above synthesis a UGC gas freed from CO_2 and sulfur, made both with enriched and an air blast.

Synthesis of organic substances by the Kölbel and Engelhardt method [4] is very similar to the Fischer-Tropsch process in the conditions and catalysts, but differs from the latter in that steam is used in place of the hydrogen: $3CO + H_2O \rightarrow (CH_2 <) + 2CO_2$.

As a result of this, the stage of preliminary conversion of carbon monoxide with steam to produce hydrogen is avoided, which greatly simplifies the process as a whole. Concentrated carbon monoxide is not necessary for the synthesis, which proceeds with a high degree of conversion even when the CO is strongly diluted with other gases, for example CO_2 and N_2. Performance of the above synthesis with UGC gases will enable us to avoid adjustment of the process to produce hydrogen from other sources. This synthesis with the use of a cheap iron-copper catalyst has been developed in detail at the IGI [5]. The following optimal conditions of synthesis from CO and steam were found, for an average pressure of 10 atm and a reduced iron catalyst: temperature 200-220°C, volume velocity 80-100 ℓ/ℓ catalyst/h. The degree of the conversion of the carbon monoxide under these conditions is about 70%. Out of the CO entering into reaction, about 83% goes on the synthesis and 17% on the conversion reaction. The yield of the product is 100-110 g/m^3. Hydrocarbons are the principal constituent of the synthesis products. The synthesis is of major interest and in our opinion can be used with UGC gases.

Another very promising application of UGC gas is its use in the conversion process of natural gas. The chemical industry is nowadays using large quantities of synthesis gas composed of carbon monoxide and hydrogen. These gases are most conveniently obtained from natural gas by reacting the latter with oxygen and steam. A mixture of carbon monoxide and hydrogen in a ratio close to 2:1 is then produced. However, for many organic syntheses the H_2:CO ratio in the synthesis gas must be about 1:1.

To increase the CO content in the methane-conversion gases, carbon dioxide is often added to the starting methane-oxygen mixture, which at high temperatures reacts with the methane according to the scheme:

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

As already noted, UGC gas contains a high proportion of carbon dioxide. It can be used as a raw material source for increasing the yields of hydrogen and carbon monoxide, gases for chemical syntheses. The most valuable components of the UGC gas, hydrogen and carbon monoxide, can be successfully utilized at the same time.

Thus, at those Podzemgaz stations where natural gas can be delivered, and oxygen is available, successful chemical syntheses could be carried out on the basis of the conversion gases of natural gas. The UGC gas can serve as an auxiliary raw material for increasing the yields of components of synthesis gases, and also as a source of heat.

There are two methods for the conversion of natural gas -- catalytic and thermal. In the catalytic method the process is conducted at around 800°C, but far-reaching purification of the gas from sulfur compounds is necessary.

In the thermal method the process is carried out at temperatures not lower than 1200°C, but purification of the gas from sulfur is not obligatory.

UGC gases usually contain a large amount of hydrogen sulfide, sometimes reaching 3%. The selection of the conversion method should in each case be made after technical and economic calculations on the two variants of the process. To facilitate this selection, we calculated the possible yields of the desired products under the conditions of chemical equilibrium, because at high temperatures this is established fairly rapidly.

In the calculations we used two equations:

$$H = 2x + 2Ky \qquad (1)$$

$$C = x + y \qquad (2)$$

where H and C are the numbers of moles of hydrogen and atoms of carbon in 100 moles of the starting mixture, x is the amount of hydrogen or CO in moles per 100 moles of the starting mixture, y is the number of moles of CO_2, Ky is the number of moles of steam, and K is the equilibrium constant of the water gas reaction.

The calculations by eqs. (1) and (2) were done on the basis of utilization of UGC gas having the following percentage composition: H_2S 1.9, CO_2 28.4, C_mH_n 0.4, O_2 0.2, CO 15.6, H_2 35.6, CH_4 1.8 and N_2 15.7. The results of the calculations are shown in Table 1.

As can be seen, with increasing conversion temperature there is a sharp fall in the yield of the ballast components and a rise in the contents of CO and H_2.

To estimate the heat expenditure on the oxygen conversion of mixtures of natural gas with UGC gas, conversion was calculated for gas having the following composition (in vol-%): H_2S 2.4, CO_2 40.2, C_2H_4 0.2, O_2 0.5, CO 9.5, H_2 16.8, CH_4 1.6, and N_2 28.4.

Table 1. Equilibrium yields of components in the oxygen conversion of mixtures of UGC gas and CH_4

Temp., °K	CH_4:UGC gas ratio	Yields in moles/100 moles starting mixture:			
		CO	H_2	CO_2	H_2O
1300	0,5	30,3	30,3	31,1	62,7
1300	0,25	40,3	40,3	17,0	31,3
1400	0,5	41,9	41,9	22,5	51,1
1400	0,25	46,0	46,0	11,3	25,6
1500	0,5	47,7	47,6	16.8	45,4
1500	0,25	48,9	48,9	8,4	22,7

When this gas is mixed with methane in ratios of 1:1 and 2:1, the resulting mixtures will have the following compositions (in g-moles):

UGC gas:CH_4 ratio	CH_4	CO_2	C_2H_4	O_2	CO	H_2	N_2
1:1	50,8	20,4	0,1	0,2	4,9	8.6	14,5
2:1	31,4	27,3	0,1	0,3	6,5	11,5	19,4

Complete conversion of these mixtures requires 52.2 g-mole of O_2 in the first case and 16.7 g-mole in the second.

The heat of reaction at a process temperature of 1500°K is 3507 kcal in the first case and 702 kcal in the second. The expenditures of heat on raising the components of the starting mixture to the process temperature are respectively 1237 and 911 kcal. This ratio shows that when the UGC gas-methane ratio is 2:1 the heat of reaction and the heat expenditure are similar and the process can take place autothermally.

The yields of the products for the two ratios considered are given in Table 2.

Table 2.

UGC gas:CH_4 ratio	Yields of products (g-mole) :				
	CO	H_2	CO*	H_2O	N_2
1:1	56,2	56,2	20,1	34,2	14,5
2:1	61,3	61,3	7,2	19,4	19,4

* Translator's note: CO_2 ?

Thus, with the gas ratio of 2:1 the contents of the ballast components in the gas obtained are reduced to a minimum.

For convenience of calculations, the yields of the gas components under the conditions of autothermal regimes at 1500°K are given in Table 3, in volumes per 100 volumes of the starting mixture. The differences in the UGC gas:methane ratio are determined by the conditions of the production of the UGC gas (amount of steam added to the blast).

Table 3. Yield and composition of gases from the oxygen conversion of mixtures of methane with UGC gas

UGC gas:CH_4 ratio	O_2 consumption, $m^3/100\ m^3$ starting mixture	Yield of gas components, $m^3/100\ m^3$ starting mixture				
		CO	H_2	N_2	CO_2	H_2O
1,60	29,0	59,8	59,8	17,8	11,6	31,4
2,0	26,0	52,0	52,0	24,7	11,0	29,6
2,4	22,5	52,3	52,3	21,7	9,7	26,3

Table 3 shows that on taking 66 volumes of UGC gas and 33 volumes of methane we can get 100 volumes of a mixture of equal parts of CO and H_2.

For practical working through of this question technical and economic calculations must be done on the consumptions of raw material, materials, and energy for a station of known gas output (e.g. the Lisichansk UGC station), the basic scheme of the installations for the conversion of natural gas must be developed, and laboratory tests must be carried out on the conversion with gas mixtures corresponding to the composition of the UGC gas.

The above review of the methods of possible utilization of UGC gases for technological processing indicates that the gases can be used most effectively in the case of a complex processing of all their constituents. This would allow economies on gas compression, transportation, and purification.

As a possible way of direct utilization of the gas without its separation into components we can point first of all to the conversion of natural gas into synthesis gas by the CO_2 in the UGC gas. This process can evidently be autothermal, i.e. it does not require a supply of external heat.

Another tempting way of direct utilization of UGC gases after sulfur removal and washing out of the CO_2 is methanol synthesis, but in this case the gas must be compressed to pressures of the order of 200 atm. This process can have prospects of industrial application if the residual gas after methanol synthesis, freed from CO, goes to further processing under the same pressure.

Such further processing could be the synthesis of ammonia. Another pathway toward the solution of this problem is a search for conditions of conducting the methanol synthesis under a lower pressure, of the order of 100 atm. For this, laboratory and pilot-scale tests are required.

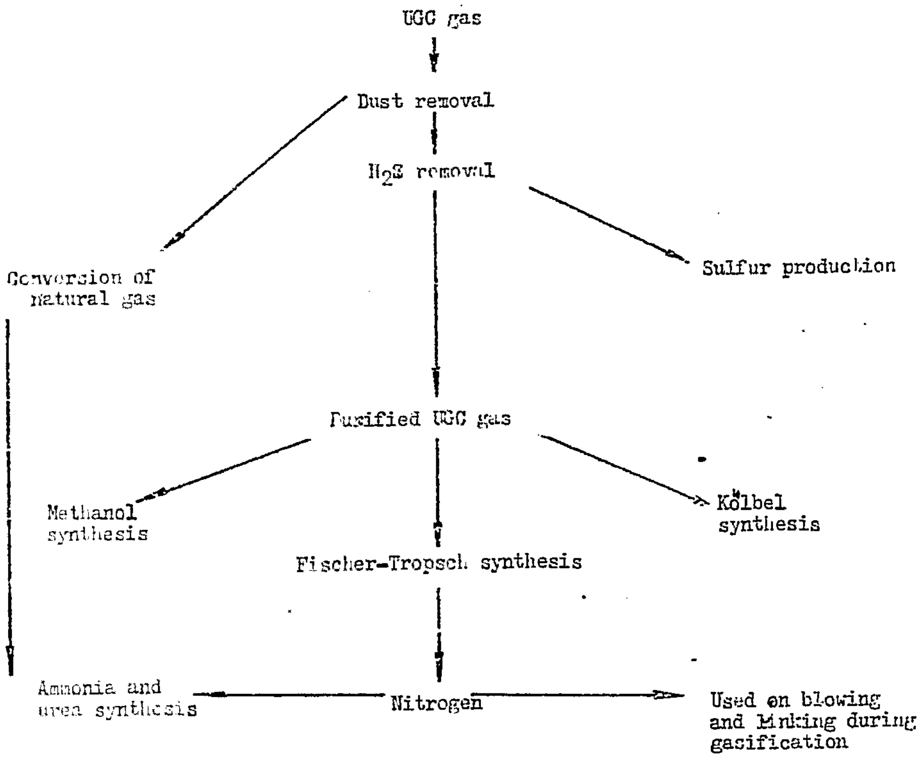
The most accessible method of direct utilization of UGC gas for organic synthesis is the synthesis of hydrocarbons and oxygen compounds by the Fischer-Tropsch method. In UGC gas freed from carbon dioxide the ratio of CO and H_2 fully corresponds to the ratio required for synthesis. This process is carried out at the comparatively low pressures of 10-20 atm and gives sufficiently good yields even with strongly diluted gases. However, the prospects for the application of this synthesis will depend much on the utilization of the synthesis products.

The high CO_2 content of UGC gas makes it possible to recommend the latter's use for urea synthesis. For this purpose it is only necessary to supply the ammonia, or to make it on the spot; conversion of the CO_2 has already been fully developed industrially and presents no difficulties.

If the UGC gas will be processed into ammonia, its purification from the carbon monoxide will be necessary. This can be done by conducting the methanol synthesis with poor gas by the Makaróv-Nizyaev method.

The above list of the possible utilizations of UGC gas components shows yet again that the latter's processing should be complex. The figure illustrates a possible scheme for the complex utilization of UGC gases.

From this it may be concluded that since the UGC gas components suitable for organic synthesis are present in the gas in small amounts, the synthesis of organic substances cannot play the main part in the technological processing of UGC gases -- it can only be an auxillary aspect.



Scheme for a complex processing of UGC gases into chemical products

The most realistic scheme of complex processing of the gas is as follows. The principal aim is ammonia synthesis. The carbon dioxide washed out is utilized on urea synthesis. Nitrogen is freed from CO by methanol synthesis by Makarov's method.

In this variant, as in others, the plant will be short of hydrogen, and other sources of this gas must be looked for. Combination of the utilization of UGC gas with conversion of natural gas may supply all kinds of UGC gas processing with hydrogen.

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