

Mechanically Activated Chemical Conversion of Gaseous Hydrocarbons

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Abstract

Propane-butane gaseous mixtures were subjected to mechanical treatment in centrifugal ball mill in the absence or presence of some mineral particles. It was found that the composition of gas mixture was changed significantly depending on duration of the mechanical coercion and solid or porous nature of mineral additives. The mechanical treatment of light hydrocarbons in the presence of quartz particles at the temperatures not exceeding 100°C resulted at long last in complete conversion of initial organic compounds to methane, hydrogen and small amounts of carbon. The same alterations of gas composition were lesser profound when the mechanical treatment was carried out in the absence of minerals or in the presence of porous silica gel or aluminum oxide.

It have been shown that direct transformation of mechanic energy to intramolecular energy of hydrocarbons is more responsible for their destruction during the process considered rather than catalytic properties of the minerals.

The removal of heavier hydrocarbons from natural or casing-head petroleum gas by means of MA treatment permits to facilitate further gas transportation and to improve essentially its heat-physical properties, namely, to decrease gas average molecular mass and specific gravity and to increase its calorificity and Wobbe number' values.

Introduction

It is well known that hydrocarbons (HC) C₃₊ in natural and associated petroleum gases can condense or form solid hydrates by pressure and temperature changes and, especially, in the presence of water, impeding the transportation and storage of the gas. One way to prevent these undesirable effects is a removal of liquefying and hydrate-forming components from a gas mixture. To achieve this purpose the gases mentioned are usually subjected to low-temperature fractionation at special gas-plants [1].

An analysis of available data concerning with the applications of mechanical activation (MA) processes (*e.g.* [2,3]) allows us to rely upon the opportunity to use them for solving fore-mentioned problem, *viz.* for converting some of initial gas components either into liquid or, on the contrary, into lighter gaseous HC's.

The main purpose of this work was to estimate

possible effect of the MA on the conversion of gaseous HC's for further application of mechanical energy in the processes of preparation of natural and casing-head hydrocarbon gases for their transportation and utilization.

Experimental

As the main subject of the study we had chosen some mixtures of ethane, propane, iso- and n-butanes, iso-butane being the dominating component. Air-dry silica gel ASM grade or native quartz sand and aluminum oxide particles of 0.25-0.50 mm in size were used as mineral additives.

The silica gel and aluminum oxide were chosen as the representatives of the adsorbents having the developed external and internal surfaces. The use of quartz was due to the known fact that many of structural defects, which are necessary for an initiation of radical reactions, are producing on the quartz fresh surfaces revealing alongside with the mechanical cleavage of mineral crystals [4].

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Water-cooled activator of laboratory centrifugal ball mill of AGO-2 type was used as mechanical chemical reactor. The gas mixture examined was introduced into beforehand vacuumed reactor-activator filled by one third of its inner volume (total 80 cm³) with 8 mm milling balls. The reactor frame and the balls were made of hardened steel. 15 grams of mineral additives were introduced which also made about one third of the reactor volume. The pressure in the reactor after filling it by initial gas mixture was 1.6-2.0 bar, the temperature being not exceeding 100°C.

Initial gas mixture and reaction products were analyzed by means of gas chromatographic methods using heat conductivity detector. C₁-C₆ HC's were separated by gas-liquid chromatography in the column filled with Spherochrom impregnated by butiric ester of tri-ethylene-glycol as a stationary phase, non-hydrocarbon components (hydrogen, oxygen, nitro-

gen *e.a.*) being determined by gas adsorption chromatography in the column with zeolite CaA grade as solid adsorbent. Argon serves as carrier gas in all cases.

The mechanical activation of the reaction system was carried out for 5, 10, 15, 20 or 30 minutes at room temperature and centrifugal acceleration 60 g.

IR spectroscopy (BOMEM MB-102 IR-Fourier spectrometer), X-ray diffractometry (DRON-3 diffractometer, monochromatic Co K_α radiation), and thermal desorption of formerly adsorbed argon were the main methods of solid phase analysis.

Results and Discussion

Our experiments have shown that MA of propane-butane mixtures leads to an enrichment of reaction gas phase in hydrogen and methane and to according diminution of other HC's contents (Table 1).

Table 1

The alterations of gas composition depending on duration of MA treatment in the absence of mineral additives

MA duration, min	Content, mole %, of					
	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀
0.0	0.00	0.00	4.90	26.57	51.73	16.80
5.0	23.86	0.00	19.34	20.06	25.92	10.82
10.0	77.07	0.00	0.90	9.02	8.45	4.56
15.0	83.48	7.78	0.34	3.58	3.11	1.71
20.0	49.93	20.89	1.65	12.92	10.15	4.46
30.0	23.70	65.59	1.45	4.35	3.10	1.81

Hydrogen appears in the reaction gas composition from the MA process outset, its concentration rising very rapidly up to 80 mole % and more after 15 min of activator functioning time. At this first stage of the process, the concentrations of the main gas components, viz. C₃-C₄ HC's, decrease from the initial levels down to 1.7-3.6%. The destruction of these heavier HC molecules leads to fast formation not only hydrogen and also ethane right away from MA process starting. However, ethane molecules generated were drawn into further reactions almost at once, and their amounts in the system were lowered sharply already by the tenth minute of the process.

At the next stage of the process methane forming

reactions were developed following by according hydrogen consumption. Methane concentration increased with further prolongation the process of mechanical treatment up to 65.6 mole % 30 min after starting the process. Some part of hydrogen generated was spending, obviously, on a regeneration of certain amounts of C₂-C₄ HC's. The marked splashes of their concentrations by the twentieth minute of MA treatment can be evidence of the reactions just mentioned.

The changes of gas mixture composition were continuing still during some time after stopping the MA process and turning the reactor-activator off. During first ten minutes of exposing the mechani-

cally treated gas mixture at room temperature the noticeable increase in C_{2+} HC's contents and the corresponding decrease in the concentrations of hydrogen and methane were firstly observed. Then the trends of the concentration changes gave place to the opposite ones (Table 2).

Probably, at the end of MA treatment process a part of C_2 - C_4 hydrocarbons remains adsorbed on the milling balls' surfaces and disengages gradually during further storage.

HC destruction reactions under MA conditions accelerated significantly when the mineral particles were introduced additionally into the reactor-activator. Thus, in the presence of quartz sand additions intensive conversion reactions of initial propane and butanes developed right from start of MA treatment resulting in the forming and fast accumulating hydrogen, methane and ethane (Table 3). The most hydrogen concentration (81.8 mole %) was achieved already to tenth minute of MA process, later on it began to diminish gradually down to ≈ 60 mole %. The amount of forming methane molecules increased smoothly in the course of the whole MA treatment

process.

The gas mixture formed at long last consisted only from hydrogen and methane other hydrocarbons disappearing completely from its composition. It should be noted that final concentration of methane was much lesser and the one of hydrogen – much more in comparison with their values observed after the experiments performed in the absence of mineral additives.

The chromatographic analysis of gas mixture produced after MA treatment in the presence of quartz and further exposing the products at room temperature for 20 hours has not revealed significant changes in their composition, which is indicative of chemically balanced state of the system.

Ultimate analysis of quartz revealed that during 30 minutes of MA treatment its carbon content increased from 0.27 mass % in initial sample up to 2.28 mass % in the mechanically activated one. IR spectra of initial quartz corresponded fully to the spectrum of crystal SiO_2 [6]. As result of the MA of quartz in hydrocarbon medium, absorption bands (a.b.) at 797-779, 694, 512, 396 and 252 cm^{-1} became less

Table 2

Temporal alterations of gas mixture's composition in the course of its keeping at room temperature after 30 min of mechanical activation

Time of gas storage	Content, mole %, of					
	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀
After MA, min						
0.0	23.70	65.59	1.45	4.35	3.10	1.81
10.0	18.52	61.15	4.25	8.16	5.38	2.54
30.0	27.68	62.36	2.36	4.28	2.13	1.19
60.0	28.09	63.03	1.39	3.79	2.34	1.36

Table 3

The alterations of gas composition depending on duration of MA treatment in the presence of quartz additions

MA duration, min	Content, mole %, of					
	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀
0.0 (initial gas)	0.00	0.00	1.85	4.94	85.69	7.52
5.0	78.47	8.60	5.69	1.04	6.20	0.00
10.0	81.80	15.33	0.27	0.64	1.95	0.00
15.0	70.88	27.75	0.30	0.36	0.72	0.00
20.0	63.50	35.88	0.20	0.10	0.32	0.00
30.0	60.43	39.57	0.00	0.00	0.00	0.00

intensive, band maximum at 1085 cm^{-1} shifted to 1092 cm^{-1} , and the bend on the front of an a.b. at 1168 cm^{-1} became less pronounced; the maximum of a.b. at 460 cm^{-1} shifted up to 469 cm^{-1} . These changes can be interpreted as indicative of the increase in quartz amorphism degree during the MA. On the X-ray diffraction pattern of quartz mechanically treated in propane-butane medium, the peaks belonging to graphite and ferric carbide appeared which testified to a generation of these substances in the course of MA process. It should be noted that the specific surface area of quartz particles has increased from $0.005\text{ m}^2/\text{g}$. before up to $23\text{ m}^2/\text{g}$. after their mechanical treatment in our experiments.

The data described could be interpreted as indicative of high catalytic activity of surface centers disclosing when crushing the quartz particles.

However, subsequent experiments have revealed that catalytic properties of the mineral play no so important role.

Thus, the conversion of hydrocarbons was going on otherwise when their MA treatment was performed

in the presence of silica gel particles possessing not lesser catalytic activity compared with quartz. In the case of silica gel addition, the complete destruction of $\text{C}_2\text{-C}_4$ molecules was not observed for the space of the whole MA process; their concentrations in the gas mixtures obtained decreased gradually during first twenty minutes (Table 4). Then the recession in the HC's amounts ceased, and the gaseous phase began to enrich by all these components.

The amounts of hydrogen formed on the middle and late reaction stages were significantly more while those of methane were much lesser than in the experiments performed in the absence of mineral additives or in the presence of quartz. The increase of HC's concentrations by the end of the MA process was obviously caused by their disengaging from the pores in solid structure. Hydrogen content of gas mixture during first half of hour of its exposing at room temperature after mechanical treatment raised and only then began somewhat to lower, whereas the $\text{C}_1\text{-C}_3$ concentrations lessened smoothly for the whole of exposure period (Table 5).

Table 4

The alterations of gas composition depending on duration of MA treatment in the presence of ASM grade silica gel particles

MA duration, min	Content, mole %, of					
	H_2	CH_4	C_2H_6	C_3H_8	i- C_4H_{10}	n- C_4H_{10}
0.0 (initial gas)	0.00	0.00	2.14	6.95	83.02	7.89
5.0	56.05	1.64	1.29	5.36	28.03	1.79
10.0	76.33	2.51	0.82	4.37	13.63	2.36
15.0	83.80	3.02	0.46	2.78	8.75	1.22
20.0	89.57	4.11	0.18	1.54	3.70	0.90
30.0	72.12	16.91	0.91	2.52	6.43	1.11

Table 5

Temporal alterations of gas mixture's composition in the course of its keeping at room temperature after 30 min of mechanical activation in the presence of ASM grade silica gel

Time of gas storage	Content, mole %, of					
	H_2	CH_4	C_2H_6	C_3H_8	i- C_4H_{10}	n- C_4H_{10}
After MA, during						
0.0 min	72.12	16.91	0.91	2.52	6.43	1.11
10.0 min	85.60	7.40	0.28	2.21	3.84	0.92
30.0 min	90.38	4.74	0.26	1.30	2.68	0.68
60.0 min	89.26	4.17	0.22	0.81	4.83	0.72
20 hours	85.63	4.06	0.19	0.69	8.39	1.03

As a whole, the results obtained in the experiments with silica gel were more resembling those observed in the absence of mineral particles. A desorption of heavier HC's resulted in the rise of butanes' contents of gas phase only after exposing the system for one hour and longer.

IR spectrum of the initial silica gel used was corresponding in full to the spectrum of hydrated silicon dioxide – $\text{SiO}_2 \cdot n \cdot \text{H}_2\text{O}$ [6]. Since after 10 minutes of MA treatment of silica gel in the hydrocarbon medium the following changes in the spectrum had taken place: an absorption band (a.b.) at 955 cm^{-1} shifted to 940 cm^{-1} , and one at 1088 to 1091 cm^{-1} . Judging on absorption at 1632 and $3442\text{--}3426 \text{ cm}^{-1}$, water content of silica gel decreased. The absence of more significant changes in the IR-spectrum of the silica gel denoted that new compounds were not generated during the MA. The carbon content in the mechanically treated silica gel samples increased from the initial $0.67 \text{ wt.}\%$ up to 0.77% . It should be pointed out that the specific surface area of silica gel decreased from 860 to $106 \text{ m}^2/\text{g}$. after the MA, which was not predictable. The X-ray analysis has not revealed any differences between the initial and mechanically treated silica gel samples.

Similar effects of reaction intensity recession were observed when high-porous aluminum oxide particles were introduced into reactor-activator instead of silica gel ones.

These results make it clear that mechanical en-

ergy of moving milling balls effectively transforms into internal energy of gaseous hydrocarbon molecules sufficient for breaking C–C and C–H bonds when solid quartz sand particles are present in the reactor. Energy impulses originating from the collisions of metal balls with porous mineral particles perceiving (and extinguishing) only by mineral lattices and are not converting to intramolecular energy of organic molecules sealed in the pores.

The removal of heavier hydrocarbons from natural or casing-head petroleum gas by means of MA treatment is a way not only to facilitating gas further transportation and besides to essential improvement of its heat-physical properties. Calculation data given in Table 6 show that the alterations of initial gas compositions leads to a significant decrease in gas average molecular mass and specific gravity and to a great increase in gas calorificity and Wobbe number' value. These alterations were more greater and faster when MA treatment was performed in the presence of quartz sand additions than in the absence of any mineral particles. Optimal duration of MA treatment of propane-butane mixtures under the working conditions of ball mill used was about 10 minutes in the former and 15 minutes in the latter cases. The effect was reduced by further prolonging MA process.

Conclusions

The energy disengaging by moving steel balls'

Table 6

The principal physical and heat producing properties of gas mixture depending on duration of its MA treatment in the absence of mineral additives and with quartz sand additions

Indices	Value after MA treatment during					
	0 min	5 min	10 min	15 min	20 min	30 min
In the absence of mineral additives						
Average molecular mass, a.m.u.	54.96	37.64	13.76	7.57	19.53	16.40
Specific gravity, g/dm^3	1.895	1.298	0.475	0.261	0.674	0.566
Lowest calorificity, kkal/kg	14170	14540	16780	19500	15600	15680
Lowest Wobbe number, kkal/kg	10290	12760	24350	38170	19000	20840
In the presence of quartz sand additions						
Average molecular mass, a.m.u.	59.26	8.92	5.67	6.58	7.35	7.58
Specific gravity, g/dm^3	2.044	0.308	0.195	0.227	0.254	0.262
Lowest calorificity, kkal/kg	14130	18520	21410	20020	19180	18930
Lowest Wobbe number, kkal/kg	9880	33370	48480	42020	38060	36980

collisions in gaseous hydrocarbon medium is sufficient to break C–C and C–H bonds in organic molecules. Thus, mechanical treatment of propane-butane gas mixture leads to a conversion of hydrocarbon molecules and at long last to their destruction to hydrogen, methane and carbon. These destructive reactions are accelerated significantly when solid quartz particles are introduced into the reaction system, and after mechanical treatment during 30 minutes hydrogen and methane become the only components of gaseous phase. In spite of larger specific surface area of high-porous ASM grade silica gel and aluminum oxide, the conversion of hydrocarbon molecules sealed within pore spaces in the frameworks of these adsorbents proceeds much more slower than on the quartz particles and even in the absence of any mineral additives. It is obvious that direct transformation of mechanic energy to intramolecular energy of hydrocarbons is more responsible for their destruction during the process considered rather than catalytic properties of the minerals.

The MA treatment of natural or casing-head petroleum gas permits to remove from gas mixtures all hydrocarbons heavier than methane and to improve significantly the operational and heat producing properties of fuel gases.

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