Standard Oil Company

(Indiana)

API-TOM Reel 82, Frames 4974-5021
About the Activation of Methane Through High Pressure
(Summary of Presentation of Experiments Carried Out in the Years
1935-1941, Concordia Plant 17-7 in Oberhausen, Rhineland.

Theory

It is known that gases become reactable upon influence of heat.
The velocity of such a reaction can be sharply increased in the presence
of catalysts. Thus a reaction that can hardly be measured can run with
a considerable speed.

The idea of Slatineamu states that gases can also become reacting
by high pressure in place of heat. Thereby, the reaction occurs already
at relatively low temperatures. Thereby one obtains a great advantage
with regard to apparatus technique. The idea is based on the fact that
in high pressures the gases deviate severely from the ideal gas laws.
The gases follow, in the ideal situation, the law by Boyle-Mariotte
$p = \frac{RT}{V}$ but they follow this equation only approximately up to pressures of
a few hundred atmospheres but then considerable deviations occur. Therefore,
one must set the equation as follows:

$$p = \delta \frac{RT}{V}$$

whereby δ is a positive number and depending upon p and T. Bridgeman
has found the following form for this equation:

$$p = \frac{RT}{V} + \frac{\beta}{V^2} + \frac{\gamma}{V^3} + \frac{\delta}{V^4} + \ldots\ldots$$

wherein $\beta = RT \cdot B_0 - A_0 - \frac{Rc}{T^2}$

$\gamma = RT \cdot B_0 + A_0 a - \frac{Rc}{T^2} B_0$

$\delta = \frac{Rc}{T^2} \cdot B_0 b$

the constants a, b, c, A_0, B_0 are determined for a series of gases; beta,
gamma, delta are therefore only dependent on the temperature.

For instance for methane the deviations from the ideal gas state
can be clearly seen in Figure 1. The curve picture shows on the ordinate
the ideal and real pressures measured in atmospheres. They occurred in
a closed pressure space of one liter contents when definite amounts of
methane measured in liters were forced into that space. These amounts
are recorded on the abscissa. First one recognizes that the actual pressure

is smaller than the ideal one, that the curves cross at about 455 atm., but that then however the actual pressure increases more than the ideal one. If for instance one forces about 670 liters of methane into a pressure space of 1 liter, one has an ideal pressure of 670 atmospheres. In reality, the pressure is at 1000 atmospheres and if one compresses about 870 liters of methane then one does not have the ideal pressure of 870 atmospheres but an actual pressure of 2000 atmospheres.

Thus, the compressibility of gases is reduced with high pressures. The resistance which the various gas particles offer against the others is increased also by comparison.

Slatineanu assumes that the pressure which is conducted on the methane molecules in that manner leads to a deformation of their construction. The depolarized molecule is supposed to go into the polarized state. By the mass action a H atom splits out of the CH_4 and a methyl residue remains. The methane should thereby become reactable. H and CH_3 go into reaction with other substances. He considers the deviation in behaviour of methane from the ideal gas state as a measure for the reaction capacity. If the pressure rises over 600 atmospheres the methane is becoming more reactable with pressure. The methane is supposed, for example, to go into reaction with oils.

Let one consider such a reaction from thermodynamics, and the equation $C_{15}H_{32} + CH_4 = 2C_8H_{18}$ as the basis. If the reaction which occurs in a cleavage of the oil molecule is to be considered this would be most important in practice. The equation which has been set up from the data of various American authors for the free energy of the above reaction as follows:

Table I

$$\Delta F = +50.150 + 55.37 \ T\ln T + 0.00845 T^2 - 0.0_65 T^3 + 440.18T \quad \text{(Francis)}$$

$$\Delta F = +37.750 + 94.3 \ T\ln T - 0.0479 T^2 - 0.066 T^3 - 639.8T \quad \text{(Parks \& Huffman)}$$
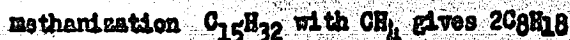
$$\Delta F = +37.998 + 100.94 \ T\ln T - 0.0495 T^2 - 0.0_5255 T^3 - 679.5T \quad \text{(Thomas, Egloff \& Morrel)}$$

for 300° to 1000° K or 27° to 727° C, one obtains the following Table:

°K	Francis	Parks & Huffman	Thomas, Egloff & Morrel
300	+13,589	+3,498	+2,425
400	+ 8,099	+1,046	+ 119
500	+ 4162	+ 15	- 600
600	+ 1496	- 88	- 511
700	- 102	+ 417	+ 269
800	- 746	+ 1296	+ 1399
900	- 546	+ 2375	+ 2693
1000	+ 405	+ 3518	+ 3948

These values are represented graphically in Figure 2. The curve shows the dependence of the free energies upon the temperature for the three equations of the authors named. One sees that the three curves are very different and are not identical in any respect. All three curves have the same form, they run through a minimum. First, the endothermic reaction becomes weakly exothermic, and then rising temperature makes it endothermic again. If one considers curve I (Francis) as a basis, then one sees that the reaction becomes exothermic at about $700^{\circ}K = 427^{\circ}C$. At about $830^{\circ}K$ which equals $560^{\circ}C$ its highest exothermic value (about 760 calories) is reached, and then it remains exothermic up to about $970^{\circ}K$ which equals $700^{\circ}C$.

A temperature range of $350-550^{\circ}C$ must be considered for the reaction with oils in practice. If one compares this range of the methanization with the hydrogenation and the cracking of the oil one should use the following equation as a basis:

methanization $C_{15}H_{32}$ with CH_4 gives $2C_8H_{18}$

hydrogenation $C_{16}H_{34} + H_2$ gives $2C_8H_{18}$

cracking $C_{16}H_{34}$ gives $C_8H_{18} + C_8H_{16}$

The equation of the free energy for the methanization according to the data of Francis was already mentioned above. The two corresponding other equations with regard to the values of Francis are as follows:

Table II

Hydrogenation $\triangle F = 42,500 \quad 67.20 \text{ T} \ln T - 517.8T$

Cracking $\triangle F = 46,560 \quad 33.6 \text{ T} \ln T - 299.5T$

The valuation is as follows:

$^{\circ}K$	C_6	Methanization	Hydrogenation	Cracking
625	352	+999	-10730	-5540
650	377	+583	-11150	-6630
675	402	+206	-11500	-7845
700	427	-102	-11800	-9010
725	452	-339	-12020	-10140
750	477	-518	-12200	-11280
775	502	-648	-12310	-12310
800	527	-748	-12370	-13360
825	552	-760	-12370	-14580

From the table one can see that the methane reaction has much less heat graduation than the hydrogenation and the cracking.

The free energy as connected with the reaction constant K by the equation $\Delta F = RT\ln K$. Thus one can calculate the yield of C_8H_{18} related to charged oil for the gas phase by using the mass action laws for the three reactions.

From the mathematical formulation, one can see that the yield of C_8H_{18} in the methanization and hydrogenation is independent upon the pressure but dependent upon the temperature. In the range from 625°K to 825°K or 352°C to 552°C the following yields of C_8H_{18} were obtained for the methanization and hydrogenation, calculated on charged oil.

°K	°C	Methanization	Hydrogenation
625	352	26.95%	97.41%
650	377	30.67%	97.04%
675	402	34.03%	97.30%
700	427	36.73%	97.20%
725	452	38.71%	97.01%
750	477	40.11%	96.77%
775	502	41.08%	96.46%
800	527	41.67%	96.07%
825	552	41.58%	95.60%

These yields relate to the molecular ratio 1:1. One molecule CH_4 or H_2 reacts with one molecule of liquid hydrocarbon. The yields in the hydrogenation are very favorable while those in the methanization are small. Here first the yield of C_8H_{18} calculated on charged oil becomes considerably better when the molecular ratio is shifted in favor of the gas, that is, with a rising partial pressure of methane. The calculations from the mass action law show, for instance, at 700°K, which equals 427°C, for a molecular ratio oil:gas = 1:1 to 1:1000, the following:

Mol. Ratio	1:1	1:10	1:100	1:1000
Methanization	36.75%	66.83%	90.18%	101.56%
Hydrogenation	97.20%	99.03%	99.46%	99.12%

Only with excess of methane the yield of C_8H_{18}, expressed on the charged oil, rises considerably. In the hydrogenation a gas excess does not influence the yield considerably.

The amount of added-on methane, calculated on charged oil, rises from 2.6% for the molecular ratio 1:1 to 7.12% for the molecular ratio 1:1000, that is, in the first case 102.6% in the second 107.12% of liquid products would be recovered. With rising methane pressure the value approaches a theoretical limitation of 107.55%.

Further, one can see from the mathematical formulation that the yield in the cracking depends on pressure and temperature, even though only a small extent upon either of them. The following table results:

$^\circ K$	$^\circ C$	1000 Atm.	Cracking 200 atm.	50 atm.
625	352	90.34	97.82	99.44
675	402	97.49	99.48	99.87
725	452	99.29	99.88	99.96
775	502	99.73	99.95	99.99
825	552	99.89	99.98	99.99

The yields of $C_8H_{18} + C_8H_{16}$ calculated on charged oil is just as favorable the cracking and for the hydrogenation.

As we have seen, the methane reaction runs only slightly exothermic. Slatineanu has tried repeatedly to increase this weak exothermic action by allowing a strongly endotherm reaction to run along side, for instance, the hydrogenation or the water formation from hydroxyl-containing hydro-carbons. If one admixes 20% H_2 to methane, then according to the mixing-law the free energy of the total reaction at $452^\circ C$ is about -2,700 calories. For this one must, of course, assume that the two reactions run with the same speed. One assumes here that the hydrogen would activate the methane so that both reactions would run equally fast.

One assumes in all these considerations that at each temperature and each pressure the reaction would go on according to the formulas stated. But in reality this is not true. As it is known from cracking, the cleavage of hydrocarbons occurs more and more towards the center with rising pressure. But with rising temperature the cleavage point travels towards the end (compare Heinze "New Processes for Refining of Fuels". 2nd Part, 1934, page 15).

Therefore, these thermodynamic calculations give only very weak indications for the actual occurrences. The experiment must decide about these.

Importance in Practice

Nevertheless, it was of use to treat these ideas also in practice and to test their realizability. If one could realize them one would have done an important work for chemistry. First of all the methanization would have been a new chemical reaction, second place, other gases than methane could have been tested for their reactability under very high pressures. Thus, a wide field of study would have been opened. The methanization proper would not have stopped with hydrocarbon chemistry but would have past over to other fields of organic chemistry and would have gone over into their practical use. For the hydrocarbon chemistry particularly the motor fuel synthesis, there exists a hope that through methanization side-chains could be introduced to hydrocarbons. These would yield knock-resistant naphthas. In practice oils that are difficult to process are to be split into such naphthas.

Slatineanu claimed in the patents that not only the petroleum products, tars and oxygen containing organic compounds but also coal, lignite, peat, bitumens, asphalts, cellulose and rubber could be treated with methane in presence of a liquid phase. He also plans to convert $CO-H_2-CH_4$ mixtures into various hydrocarbons. Thereby, he has the opinion that an endothermic basic reaction could be realized by simultaneous course of an exothermic steering reaction.

Therefore, it was necessary in every case to look into these ideas and experiments had to be carried out in this direction.

Experiments

One can test the reactability of methane under very high pressures, by allowing methane to act on an unsaturated hydrocarbon, for instance, hexene. Similarly as hexene through hydrogenation goes into hexane it would have to be converted into heptane by methanization. Unsaturated compounds with fewer C atoms were eliminated because they go of themselves into polymerization.

Since such olefins are difficult to obtain in sufficient amounts, it is enough to use strongly unsaturated kogasin of the Fischer-Tropsch synthesis or an unsaturated cracked naphtha in the reaction with methane. In both cases saturated products should be formed.

This effect ought to be reached also by oil splitting. Similarly as the destructive hydrogenation of oil furnishes unsaturated naphthas, this should also be the case with corresponding destructive methanization. Since this is the only case which needs to be considered for the practice, it was also the only one which was considered by thermodynamics. It was also studied most in practice by us.

For the evaluation of the experiment, it is necessary to convert a heavy oil mostly into light naphthas which are to be saturated. The total amounts of all end products with a C number of 2 upward must be always larger than the charged oil quantity. Methane causes a distinct weight increase through addition, in contrast to hydrogen in the hydrogenation. The naphtha must be knock resistant.

A. Experiments of Slatineanu 1935-1938

1) Experiments with acetylene-methane (15 experiments Jan. to Mar.1935)

Slatineanu based his experiments on a presented thesis about "Experimental studies about thermal cleavage of methane in presence of carbon, unsaturated hydrocarbons or nitrogen" of April 14, 1934. He carried out demonstrations with a small high pressure tube with acetylene-methane mixtures at pressures up to 250 atm. and temperatures up to 350°C. The thesis mentioned formation of liquid hydrocarbons. This was not confirmed by the experiments. Soot (carbon) was formed, and the apparatus was clogged up.

2) Experiments in Plant A (50 experiments March to Nov. 1935)

He only started in March 1935 the demonstration of his "methane high pressure process"---/the work with high methane pressures. A small high pressure apparatus with a reaction vessel of 1 liter content was finished in the meanwhile. This apparatus could attain pressures up to 1000 atm. and temperatures up to 370°. Probably the temperatures were still higher since the measuring possibility was lacking. Methane was reacted with paraffin oil, tetraline, naphthalene, methanol, tar, vaseline and fat in amounts of about 0.5 kg. of catalyst, whose composition and preparation were kept secret by him. For this purpose the catalyst was built into the reaction space and possibly reduced. After the reduction the substance which was to be tested was filled in, in liquid or dissolved form, and the apuratus was set on temperature. One allowed methane to flow through the apparatus under pressure from the four separation bottles of the compressor. The liquid products were collected in a separation vessel. The portion which was not condensed passed into an electro filter and an activated carbon tower. The end gas was conducted into the outside by a gas meter.

The first 22 experiments with methane and the 3 with admixture of ethylene could only be evaluated qualitatively because of apparatus defects. More or less cleavage occurred in the charged liquid product. Only a few which were evaluated for demonstration purposes were set up in a balance sheet. In March and April 1935 two experiments (A6 and A11) had a positive balance, i.e., an increase of the charged liquid over 100%, namely, once with paraffin oil at 750 atm. and 290-320°C with 3%. The gaseous products which were formed were not considered. Two further continuous experiments (A40 and A41) which were carried out in August 1935 with large amounts of paraffin oil at 800-1000 atm. and 340 to 370°C also gave a positive balance of plus 3% and plus 11% by calculation of the gaseous products which were formed. Thereby, in the last experiment one obtained 1% more liquid than was charged. From these results it was concluded that the weight increase actually was caused by the addition of methane to oil cleavage particles.

In May and June 1935, Slatineanu carried out 5 experiments (A20 to A24) with carbon monoxide and water and CO-H₂-CH₄ mixtures in order to prepare formaldehyde. Thereby he used pressures of 300-1000 atms. and temperatures from 150-350° and various catalysts. The experiments were negative, only carbon dioxide and hydrogen was formed.

From June till the beginning of July 1935 he carried out 10 experiments with vaseline and CO-H₂-CH₄ and CH₄-H₂ mixtures and methane itself. These yielded naphtha indeed. The proof of the methane addition could not be carried out. The first experiment in August 1935 (A39) with a CO-H₂-CH₄ mixture and paraffin oil with reduced copper oxide as a catalyst, and pressures of 700-950 atm., and temperatures of 300-322° showed again a positive balance. There occurred an increase of the charged liquid product by 8.6% without consideration of the gases that were formed.

In October and November 1935 Slatineanu undertook a number of experiments in order to realize the "steered reaction" with $CO-H_2-CH_4$ mixtures. Pressures were up to 1000 atm. and temperatures up to 350°. Also a gas circulation pump was used now. Catalysts were $Fe_2O_3-MOO_3-NaCl$, $MgO-MOO_3-Fe_2O_3$, $NiO-Al_2O_3$ (Schustan). No naphtha was obtained however.

3) Experiments in Plant B (1 experiment Nov. 1936)

These first experiments in Plant A, of which 5 showed a result on which realization of the methane reaction was concluded, caused Slatineanu to carry out experiments on a larger scale because then the demonstration with these experiments of the workability of the "methane high pressure process" was considered as successful.

The Hofer firm, Mühlheim/Ruhr prepared a pressure container of about 15 liters content in the year 1936 in which a resistant heater was built in by the Siemens firm. The oil and gas was conducted into this heating vessel which stood upright. On this one put the unheated catalyst space of about 30 liters content which was to be brought up to the temperature by the reaction participants which entered. The apparatus of Plant D consisted also of a high pressure separator, two gas circulation pumps (Hofer) with 200 liters or 24 liters maximum stroke volume, and 2 oil pumps (Hofer) with a maximum capacity of 46 respectively 12 liters per hour. After eliminating the difficulties in the beginning with the new apparatus particularly with the heating body, an experiment was carried out in Nov. 1936. Paraffin oil with methane-hydrogen was reacted with a reduced iron molybdate catalyst. The pressure was 800 atm. the temperature in the upper portion of the catalyst space about 340° while the outer wall of the heating vessel had about 400°. Inside there were probably considerably higher temperatures.

Because of the too heavy use of the resistance heating there occurred a short circuit which caused a premature ending of the experiment. As result of the experiment, an only partial cleavage of the oil to naphtha with very good octane numbers of 74.3 were obtained. The high gum content of oil (?) to each 100 cc indicate a cracking action. Since no balance could be set up because of mechanical disturbances, the participation of methane in this experiment could not be proven.

4) Experiments in Plant E (19 experiments Dec. 1936 to Jan. 1938)

Plant D which was very unfavorable was changed, leaving off the 30 liter catalyst room which was set on top. Also the resistance heating which was not good was substituted by eddy current heating which was constructed by the High Tension Company, Köln, according to directions by Slatineanu. This eddy current heating had the form of a cylinder so that its inner hollow space was very advantageous to take up the catalyst in such a manner. The content of this space was about 6 liters.

The first experiment E-1 was considered particularly noteworthy. Oil, Shell Oil and a heavy Fischer oil were treated in sequence with a CH_4-H_2 mixture at 950 atm. and temperatures up to 400°C in presence of a reduced iron molybdate catalyst. The oils were conducted through the catalyst several times. Good yields of naphtha with very good knocking properties was obtained. An addition of the liquid product over 100% could not be determined. The hydrocarbons in gas and gasols were not at all considered. In spite of this incomplete measuring Slatineanu asserts that this naphtha was formed by aid of the methane reaction. He did not bring additional proof that we were not dealing with a cracked naphtha.

First he had different plans. One, he wanted to react a CO-H_2-CH_4 mixture into naphthas (the so-called "steered reaction"). Another time he wanted to react methanol with bensol and toluol or methanol and other hydrocarbons. Thereby, these reactions should possibly result in amines, for the gas phase contains methane and much nitrogen. The nitrogen was to be made reactable under high pressure. Further he tried to convert the methanol into ethanol and by the aid of carbon monoxide into glycerine and glycol. None of the experiments that were conducted on paper with the aid of thermodynamic consideration led to success in the practical test (E-2 to E-6). As soon as CO was present in the gas, iron carbonyl was formed which decomposed often in the reaction vessel. Iron molybdate, zinc chromate, nickel, aluminum oxide in reduced form served as catalysts at that time. The pressures were up to 900 atm., temperatures up to 450°. Since these experiments, which were only random tests with an arbitrary catalyst, were without success from the beginning. Slatineanu discontinued them for a while.

Experiment E-7 was to be the treatment of naphthas with bensol or methanol in presence only of nitrogen under high pressure. According to his theory thereby, by way of amine formation, condensation and methylization was to occur. A short circuit in the heavy current heater did not allow the experiment to be carried out.

After completion of a new eddy current heater body in June 1937, Slatineanu took up again the execution of the idea to split heavy oils like paraffin oils, Solvay oils, tar oils, shale oil, and to condense light (Trans.: naphtha?) in presence of CH_4-N_2 (this time with only 25% N_2). This experiment E-8 was unsuccessful. The balance could not be set up because the experimental arrangement with regard to apparatus was so incomplete that the light naphthas which were brought in with the heavy oils went through the oven and also through the condenser and the activated carbon and it was found partially in the gasometer. Also, the great number of the pumped-in substances formed a mixture of the various oils in the end product. A sharp separation and a clear definition was not possible at all. The gaseous products that were formed were not regarded on the whole. The gasols from the activated carbon were not measured or analyzed. Experiment A-9 with the same selection of ideas could only be started, and had to be discontinued because of failure of the installations in the oven. Nevertheless, it showed that the heavy Shell oil P43 would hardly work under 400°C and 900 atm. CH_4 pressure. This is a noteworthy contrast with the result of E-1. First one used nickel, zinc oxide, molybdate acid and iron molybdate on carriers in reduced form as catalysts in this experiment.

In Sept. 1937, Slatineanu allowed the above idea to lie again and went over to use colloidal carbon as catalyst. Possibly it might also take part in the conversion. The next experiment E-12 was to split paraffin oil, Fischer oil and anthracene (?) oil on iron phosphate catalyst in presence of methane. In experiment E-13 paraffin oil and naphthalene was to be split with reduced iron molybdate catalyst. All these experiments of Slatineanu ran negative. Overlooking that the quantitative evaluation of the experiment was not possible as has been mentioned before, the qualitative respect allowed one to recognize that paraffin oil would be split very little at 400°C and a methane pressure of 100 atm. contrary to the result in E-1.

All experiments from E-2 to E-13 deviated more or less from the actual subject, to prove the reactability of methane. Partially, they have nothing to do with it.

Since we were not convinced that the naphthas which were obtained in experiment E-1 actually originated from the methane reaction, we used the time of a vacation of Slatineanu in October 1937 to repeat the experiment with paraffin oil and CH_4 or CH_4-H_2 with reduced iron molybdate catalyst (E-14-E-16). However, we obtained only little cleavage of heavy oils as it was seen already in Experiment E-9 to E-13. A complete balance was not possible because of the deficient experimental equipment. Nevertheless, we concluded from the qualitative result in the oil in experiment E-1 had been subjected to temperatures above 400°. In comparison to a few experiments in plant A, we did not obtain more liquid products than had been charged.

Now Slatineanu remained with the simple reaction of paraffin-methane that tries to use as catalyst reduced iron oxide (E-17) which had been prepared from nitrate, and molybdate iron (18) which had been sintered at high temperatures. Neither experiment resulted in naphtha at 400°C.

Only in January 1938 he decided upon urging of the supervisory board, to repeat experiment E-1, again (E-19). The result was that cleavage to naphtha only occurred at temperatures above 400°. Therefore the temperatures in experiment E-1 had to be at least partially around 440°. The reduction of the methane pressure to 350 atm. resulted in the same cleavage as at 900 atm. Since because of apparatus reasons no balance could be set up, the question of whether or not methane had taken part in the reaction remained open again. But we were inclined to the opinion that the naphtha which had been formed in E-1 was not obtained with smaller pressure. We assumed that it was a cracked naphtha. Laboratory experiments in small pressure autoclaves in which thermal cleavage of paraffinic oil was carried out confirming our opinion. Oil is only split at temperatures over 400° to any extent.

5. Experiments in Plants G and H (11 experiments March to Dec. 1938)

All interesting questions which occur in the experiment E-19 and which required urgent clarification through control experiments remained undone because Slatineanu closed plant E because the pressures of 1000 atm. seemed insufficient to him. Plant G which was ten times as large if one bases it on the ratio of the catalyst space was finished in order to carry out the experiment at 2000 atm. pressure.

Upon suggestion of Slatineanu in the year 1936 one did not only build the half technical plant D for 1000 atm. but which according to his calculations would produce 0.5 tons of naphtha per day, but also a plant E was built for further experimental purposes. One started upon his suggestion that construction of a plant G with technical dimension for 2000 atm. pressure with an estimated capacity of 5 tons of naphtha per day.

The various parts of this apparatus were furnished and set up in the course of the years 1937 and 1938. They consist of:

One autoclave, about 700 liters contents and one high pressure separator about 150 liter content, both for 2000 atm. built by the Krupp firm in Essen.

One oil pump with a calculated capacity of about 300 liters per hour with 2000 atm. pressure. But it actually performed a tenth of that. It was prepared by the firm Balcke in Frankenthal.

Two compressors with a capacity of each 36 cu. meters per hour at 1000 atm.

One additional compressor which was to take up the performance of the two that were named before, and which was to compress the gas to 2000 atm. All three were prepared by the firm Hofer, Mulheim/Ruhr.

One gas circulation pump with about 250 liter of suction volume per hour. Built by the Hofer firm.

One gas circulation pump with about 7,500 liters suction volume per hour built by the firm Borsig, Berlin.

A eddy current heater for the autoclave and one for the high pressure separator. Each of the two heaters consist of two cylinders which contain heat coils whose radii was different by a few centimeters. The two cylinders are concentric to one another in the high pressure space. It was built by the High Tension Company in Cologne.

The valves and fixtures that belong to the high pressure pipes were furnished by the Krupp, Mannesmann and Hofer firms.

In order to operate plant G the autoclave was eventually provided with catalyst and being heated from the inside. In the separator the inner heating was left out.

Soon Slatineanu had the plan in the meanwhile to undertake preliminary experiments for plant C with the high pressure separator as reaction space, also a inner heating was built into this high pressure vessel. The change of plant C for experimental purposes at 2000 atm. brought about plans for the plants D, F, G and H. Only the plans for plant G and H were realized and the following experiment of the year 1938 were carried out in these plants.

But in the first experiments in plant G from March to July 1938 one operated only with pressures up to 1000 atm. and temperatures of only 300-350°. In this plant G there was the high pressure separator of the plant C with heating as a reaction vessel. In the vacant space of the heating the catalyst was built in. About 20 liters were used for G-1 and about 60 liters for G-4 to G-6. The inner installations of the oven which were the piping for oil and gas and thereby the moving of the reaction participants was changed by Slatineanu for each experiment. The separator of plant C of about 7 liter content which has been arranged through the strengthening of the props served as separator for the 2000 atm. Oil and gas pumps were used in all experiments except G-1.

One investigated in these experiments only the conversion of methane with paraffin oil. Thereby one added in a few cases some hydroxyl-containing hydrocarbons in the form of an alcohol (methanol or amyl alcohol) in order to initiate the reaction easier through water formation which was to be expected. The catalysis was thought of by Slatineanu in such a manner that in experiment G-1 the conversion of methane was to be carried out with alkyl chloride formation. In experiment G-3 it was to be done with amine formation. For the same purpose he used CoO-CuO-KCl-MgO-pumice catalyst in G-1, and G-3 he used gaseous ammonia dissolved in methanol and brought into the reaction vessel at the same time with the paraffin oil and the methane. The results were negative. In G-1 there came a apparative novelty. The circulation of the gas and oil in the reaction vessel was to occur without a pump, only according to a type of "thermo-syphon". The gas and naphtha vapors were to move from the warmer portion of the reaction vessel to a cooler and through this gas movement also the liquid was to be put into circulation. This idea could only be realized on a small scale with great difficulty, therefore, so much less on a large scale. Thus the liquid was only in contact with the gas to a small extent since it just remained in the reaction vessel after being pumped there.

An experiment G-2 was carried out between the two experiments which joined the thermal-syphon idea, and which was to test whether cold charged oil would need to proceed to cleavage and simultaneous methanization at 350° because of a shifting of the vapor pressure equilibrium of the hot paraffin oil which is under pressure. Hereto, great apparative difficulties were encountered. The experiment was without result.

In June 1938 the field of chemical catalysts was left after these experiments. It was still planned to react methanol with carbide in presence of methane. Since carbide contains sulfur one did not do it.

(Trans.: More detailed results are given for similar experiments).

(Frame 4993) Results and Critique to the Experiments by Slatineanu

Slatineanu has not brought clear experimental proof for the realizability of his idea. The only time in which a positive result was obtained in plant A at 1000 atm. pressure could never be repeated. A pressure of 1,650 atm. CH_4 at 400° did not cause oil cleavage.

The experiments carried out by him had the following shortcomings:

1) The apparatuses (plant B, E, D, and H) that were used were much too large for experimental purposes. He used them nevertheless because he had the wrong opinion that (a) each chemical reaction that could be made on paper on basis of thermodynamic considerations must necessarily be realized. Therefore he did not consider it necessary to do extensive investigations on a small scale. (b) he believed that the few experiments which showed positive action in plant A had to be absolutely right and did not subject it to frequent repetition and counter-proof. Thereby one would have found the mistakes sooner.

He was of the opinion that the physical-chemical conditions which are necessary for the reaction can only be produced in a large apparatus.

Since the apparatusses were too large, the experiments lead to immense difficulty. Much time, material and energy, and also much money was used which is in no relationship to the obtained observations. Since the reaction on a small scale, even if the positive results in Plant A were really true, was not worked out at all, the transposing into a large scale had necessarily to cause immense difficulties. We suggested several times to develop the reaction in a suitable small apparatus but Slatineanu would not listen.

2) Slatineanu was inclined to carry out the whole experimental program in the D (Trans.:?) plant at the same time. That is, he carried out a series of liquids and gases in various combinations one after the other through the reaction space whereby he often changed also temperature and pressure conditions. Instead of carrying out a single conversion clearly to work out the product and to make conclusions from the results, it was impossible to get clear experimental picture about the various experimental parts by his method; since particularly working with such very high pressures would cause apparatus difficulties, untightness, failure of pumps, etc.).

3) First of all the measuring of the products that are formed
is very difficult because of the large scale of the experiment, and because
suitable measuring installations are lacking for the resulting large
quantities of liquids and gases.

Slatineanu did not pay any attention to gases and gasole. In
spite of the many gas analyses which he had carried out, he could not make
any clear conclusions because the exact amounts were not measured.

Since he used different oils in the individual experiments they
could not be separated clearly, and there was some of the previous oil
always mixed in with the fresh oil. This made analytical evaluation more
difficult.

Therefore, it was not possible to set up clear balance sheets
for each experiment or experimental period in order to be able to say
that such-and-such amounts of hydrocarbons with the C number of 2 and
upwards (Gasol plus naphtha plus oil) resulted, and so-much CH_4 is consumed
or produced, from the charged amounts of oil and methane.

4) Also the experiments were not carried out in a logical series
but were single fairly interesting experiments which seemed somewhat
improbable at times. A well-planned investigation may have led to the
realization of some of the ideas.

B. Experiment of Sexauer and Winner, 1939-1941

In spite of the lack of positive results, experiments were
carried on this field by Sexauer and Winner between 1939 and 1941. They
tried to make these experiments more exact. They used the smallest
catalyst space which was available. They attempted also to set up
complete balance sheets.

............(Trans.: Several frames of detail omitted here)...........

1) Conclusions from Our Experiments

We tried out only a few catalysts and these experiments could
be continued in many possible directions. One could use other metals
like Mn, Cd, Sn, Pb, Ti, Cr or alkaline earths like Ca, Sr, Ba, Mg in
various combinations and preparation forms. Or we could test the action
of chlorides, fluorides, sulfates, phosphates, borates, etc.,or acids like
phosphoric acid, boric acid, etc. The choice of substances and combinations
which could be used as catalysts is very numerous. Also the activators
which strengthen the action of a catalyst should be investigated more
accurately. The same is true for the catalyst poison which may possibly
hinder the catalysis, like for instance sulfur in many cases.

Then, it would be advisable to choose a static arrangement in
place of a continuous arrangement for such experiments. The investigations
should be carried out more advantageously in a closed pressure space,
possibly a turning autoclave. The advantage of such an arrangement was
discussed in various ways.

But from our experiments in plants E to K we became convinced that by the negative results it is not a worthwhile task to continue the experiments. The probability that we will find a catalyst substance with a positive effect is very small. Also, the probability is very small of finding that we have not recognised a small positive effect which was in our experiments, but was not recognized in the named experimental arrangements.

According to our laboratory experiments one can carry out hydrogenation without catalysts, but the catalyst speeds up the reaction. But even with catalysts we do not see even the slightest positive indication of a methanisation which would be proof enough to stand up against convincing critique.

Therefore, we have the opinion that the positive action which has been found by Slatineanu in a single experiment in plant A was caused by an apparatus fault which cannot be found now, and which could not be reported after several trials with suitable control experiments, and several repetitions would certainly have been found at that time.

From our experiments that were carried out carefully, we conclude that methane does not become reactable under high pressure. Thus the imaginations of Slatineanu did not materialize.

Therefore, we break off the investigations on this subject upon request of the research supervisory board.

SUMMARY

There is a theoretical part and an indication of the importance for the practice of these experiments. Then the experiments which were carried out between 1935 and 1941 were discussed and conclusions were made.

1) Slatineanu did not bring a convincing proof in the years 1935 to 1938. The positive balance effect which was found a few times in the year 1935 could not be confirmed later.

2) Sexauer and Winner carried out very accurate experiments in the years 1939-41 and could not find proving evidence for the methane reaction.

3) Therefore, the positive balance effect which was found in 1935 is ascribed to experimental errors which were not recognized then, and cannot be determined at present.

4) The conceptions of Slatineanu about the activation of methane through high pressure do not occur according to the present results.

Oberhausen in the Rhineland - May 30, 1941

(Tables, apparatus drawings, and graphs follow in original)

/s/ Sexauer and Winner

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