

SOME RECENT DATA ON THE DECOMPOSITION OF FLUID HYDROCARBONS. I

Experiences Obtained on Melted-Metal Decomposer

By GY. SCHÖBEL, Mrs. A. SCHÖBEL-GILDE, L. MÉSZÁROS,
T. SZÉLL and I. GALAMBOS

Department of Applied Chemistry, Attila József University, Szeged

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The melted-metal reactor proved to be suitable for the decomposition of hydrocarbons with steam. Besides cracking a hydrocarbon-steam process takes place. The reactor can be enlarged linearly. The melt is indifferent to sulphur poisoning. From the point of view of the production of town-gas, the optimum parameters are 750 °C, longer contact time, feeding in the hydrocarbons and water in a proportion of 1:1.

Introduction

The various decompositions of hydrocarbons for the manufacturing of synthesis gas and gas additives form today an essential process of the petrolchemistry. This problem becomes the object of growing interest also in Hungary.

In the course of our work a series of experiments has been carried out with the purpose to investigate the applicability for decomposition of the melted-metal reactor developed a few years ago by the Department of Applied Chemistry. In the present paper we wish to report about these experiments.

For the oxydative decarbonylation of furfural [1] and later for various other purposes [2] melted metal catalysts have been successfully used in our laboratories. The effect of these catalysts on the decomposition of formic acid has been studied also by SCHWAB [3]. He established that the known relationship between the frequency factor and the activation energy ($B = B_0 + C/h$) is just as valid in this case as with solid catalysts. He also established that the activation energy can be reduced by the addition of a foreign metal. According to SCHWAB's judgement melted metal catalysts are very significant.

On the basis of our previous result and SCHWAB's works it was of interest to investigate in which extent the metal melts can be used for the decompositions and cracking of hydrocarbons. This problem has scarcely been studied until now; at the same time, based upon theoretical considerations and previous experiences the experiments promised to be successful.

Experimental

1. Selection of the experimental conditions and of the hydrocarbons

For the time being we had to be satisfied with the application of reactors operating intermittently with a longer contact time, being relatively far from plant-

conditions, and suitable only for the decomposition of smaller amounts of hydrocarbons. Experimental conditions and the quantity of the raw material play a decisive role in the course of cracking and thus the composition of the obtained gas. The latter is influenced also by the mode of heat transfer, *e. g.* whether the head is obtained from an outer source or by partial burning. At the selection of the parameters it had to be kept in view that the ultimate object of our experiments was the production of relatively large volumina of town gas additives.

Gasoline (boiling point below 100°C) and a mixture of pentane was selected as starting material. The decomposition was performed with steam. The decomposition of these raw materials with air has been avoided because of their low explosive limit. (Decomposing on air can be solved however, by the admixing of an inert gas. Cp. our next publication.) Disregarding the considerations on safety, however, our apparatus proved not to be suitable for air decomposition (cp. 3).

2. Description of the experimental apparatus

The apparatus is demonstrated in Fig. 1.

Water and gasoline are fed from burettes 14 and 15. Burette 15 is joined to the water feeding pump 17 by a rubber or PVC tube; burette 14 for feeding gasoline

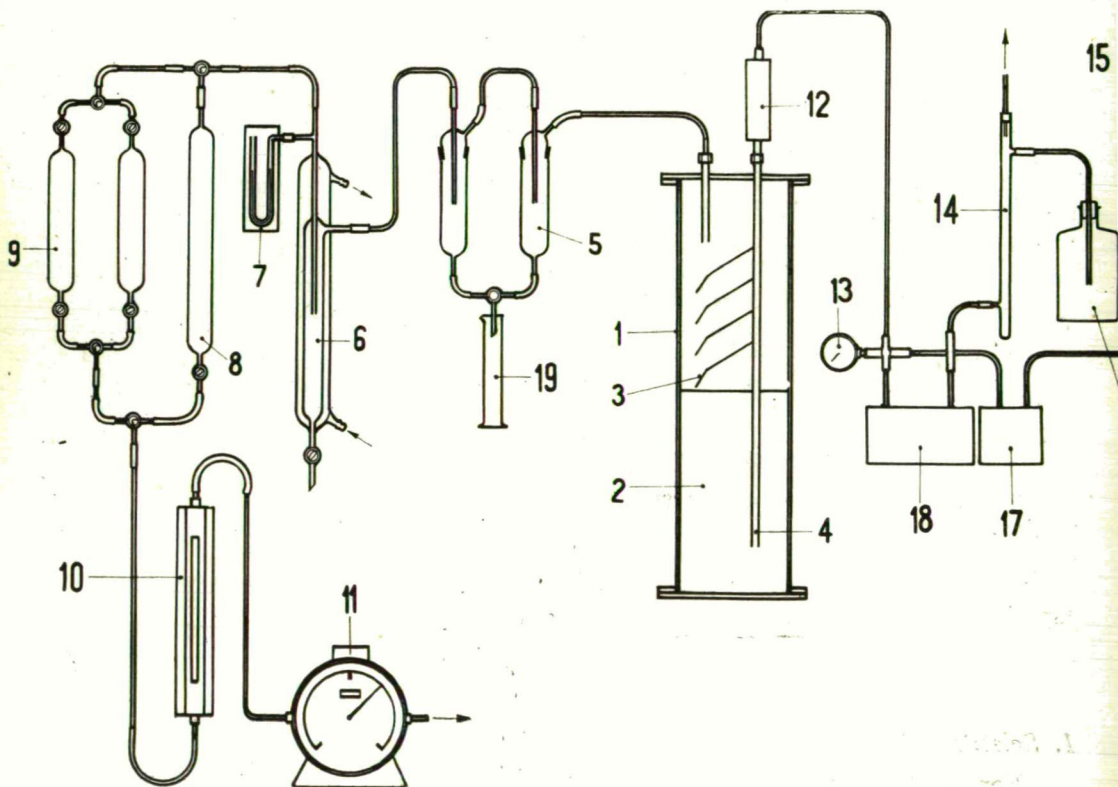


Fig. 1

(or pentane) is similarly connected to the pump 18 feeding gasoline or pentane. Refilling of gasoline is carried out by means of a vacuum pump. Feeding becomes uniform and accurate when using feeding pumps. Pressure of the pumps is indicated by manometer 13. The gasoline (or pentane) and the water get through a copper capillary tube into preheater 12. Where they are converted into vapour phase and pass through tube 4 into the reactor with a melted lead bed. By bubbling through lead 2 the gas will be cracked and is discharged at the top of the reactor. Foam catcher 3 hinders the gases to take away particles of fluid lead which would cause doggings. The gases saturated with steam get into steam dryer 5 where a considerable part of the steam separates out together with other products of low boiling temperature, formed on the course of cracking. The flowing gases get from the steam dryer into cooler 6 then from here through coal (adsorbing) column 8 or sampler 9 into gasometer 11 or into a gas-holder. The flowing velocity of the passing gas is indicated before the gas-holder by rotameter 10. Security manometer 7 belongs also to the equipment. Reactor 1 is a thick-walled cylinder of 1,05 m height, supplied with good heat insulation (pearlite) and electric heating. Lead is placed at the lower part of the reactor in the casing tube and, being in melted form, it not only ensures a good heat transfer but at the same time it acts as a catalyst too. Local overheating is considerably less in the melted bed reactor than in a solid bed reactor since in the former not only the gas but also the melt acting as a catalyst of significantly greater specific heat transfers the heat by means of conducting and streaming.

Characteristics of the reactor:

Diameter of the reactor tube: 9.5 cm
Diameter of the inner heater: 3.5 cm
Induction pipe and its immersion
into the melt — bubbling height: 50 cm.

Quantity of the lead:

Surface: 61 cm²
Volume: 3670 cm³
Weight: 42 kg.

3. Running of the apparatus

At oxydative reactions carried out at 300—400 °C used for furane-chemical purposes, the lead was oxidized by air in the lower part of the reactor and the thus formed oxide performed the oxidation of the organic compound whilst it was again reduced to lead. In the course of the present experiments carried out at higher temperatures this regeneration of the lead oxide did not ensue, thus the lead oxide and the resinous black arising from the cracking process accumulated in the system. Even for this reason we could not use air to the decomposition.

First step in starting the equipment was heating up of the reactor and evaporator at a temperature settled in the experimental plan. During the experiments the reactor was used in the temperature range of 600—800 °C and the evaporator at 250 °C with an error of ± 2 per cent. Heat control was accomplished by drop-bridle

thermoregulators controlled by a Ni-CrNi thermocouple. Air was removed from the reactor by feeding in water; feedings of the gasoline was started only after the beginning of uniform bubbling. Feeding in the liquids was carried out by means of pumps.

Feeding velocity is measured with a stop-watch, and stroke length of the pump is regulated with a micrometer screw. Constancy of feeding velocity must be often controlled during operation. The gas when bubbling through the melt will be cracked and the cracking gas passed through cyclones and a cooler and gets, while its quantity and flowing velocity are measured, into the gas holder. Maximum feeding velocity permissible on secure operating conditions was 60 ml/h of gasoline and 90 ml/h of water. At experimental series I in Table I, liquid phase was formed in measurable quantities which was determined quantitatively.

Temperature dependence of the reaction has been tested in the course of our experiments, the results are demonstrated in Table I. Variations of feeding velocity and contact time are shown in Table II while temperature dependence of the cracking of pentane in Table III.

Table I

$p = \text{constant} = 0,5 \text{ atm}$

$v = \text{constant} = 60 \text{ ml/h}$

$T = \text{variant}$

No	T	Q lit	Heating values		Analysis		Other gases	
			Kcal/N m ³	CH ₄	C ₂ H _{2n}	CO	H ₂	O ₂ CO ₂
1	600	15,5	8 000	45,9	10,3	25,2	10,0	8,6
2	660	18,5	8 066	47,4	13,6	22,2	11,9	4,9
3	700	39,4	13 667	45,6	30,9	7,8	14,0	1,7
4	735	43,3	11 227	46,9	21,8	8,0	19,6	3,7
5	800	63,0	9 602	47,3	15,4	8,0	29,0	0,3

Heating value of C_nH_{2n} was taken as 29 687.

Table II

$p = \text{constant} = 0,5 \text{ atm}$

$T = \text{constant} = 700 \text{ }^\circ\text{C}$

$V = \text{variant}$

V	Q	CH ₄	C _n H _{2n}	CO	Analysis	
					H ₂	O ₂ CO ₂
20	80,1	37,2	25,8	1,9	28,2	6,9
30	78,9	39,0	27,2	2,1	25,9	5,8
40	62,4	41,0	29,4	3,8	22,1	3,7
50	48,7	43,1	32,8	4,1	18,3	1,7
60	39,4	45,6	39,9	7,8	14,3	1,7

Table III

$p = \text{constant}$
 $v = \text{constant}$
 $T = \text{variant}$

No of experiment	Fed water in ml	Feeding velocity of water, ml/h	Fed pentane in ml	Feeding velocity of pentane ml/h	Temp. of the reactor °C	Manometer atm.	Condensed phase (ml) water	Formed gas V_0 (l)
1	100	30	100	30	600	0,5	98	25
2	100	30	100	30	560	0,5	93	43,5
3	100	30	100	30	700	0,5	85	62,5
4	100	30	100	30	700	0,5	86	61,5
5	100	30	100	30	700	0,5	83	60,5
6	100	30	100	30	735	0,5	80	69

Results of gas analyses in the Tables are given on the basis of analyses carried out on the Orsat—Pfeiffer gas analyser. Under water cooling conditions measurable quantities of organic liquid phase obtained were only in series 1 of Table I. The quantity, temperature ranges of distillation, refractive indices, and results of the elemental analysis of the organic liquid phase are shown in Table IV.

Table IV

	Q ml	Temp. °C	$n_n^{21,5}$	C%	H%
1	1,9	-71	1,3927	85,06	14,66
2	1,7	71-79	1,3970	85,03	14,31
3	1,7	79-90	1,4040	86,0	14,18

Based upon the investigation on the refractive index and the elemental analyses it has been found that the first distillate is hexane-2, the second one is hexane-3 and the third one is n-heptane-1.

Results and discussion

From the results obtained it can be established that feeding velocity is a decisive factor for the course of the reaction. On increasing the feeding velocity, that is on decreasing the contact time, the gas volume and the hydrogen content decrease whilst the amount of methane, carbon monoxide, olefine as well as the heating value of the obtained gas increase. The high heating value is not the most important factor for gas works since the heating value of the produced town gas is in general sufficiently high. On the other hand, the high hydrogen content of the gas is advantageous because of the greater gas volume and the favourable burning velocity. For this reason, from the point of view of the gas work the longer contact time seems to be more favourable. By rising the temperature until 750 °C, the total volume of the obtained gas as well as the hydrogen content of the latter are increased. This increase occurs at the expense of the hydrocarbon content which is probably connected with the fact that the decomposing process is prevailing. Consequently, from the point of view of the gas work it seems to be advantageous to hold the temperature at 750 °C.

At lower temperatures, in the condensates obtained at the end of the reaction fluid hydrocarbons appeared the boiling point of which was lower than that of the starting product. In such cases the gas formation was not uniform but abrupt.

The condensed phase formed at the end of the experiments was mainly water (see Table III); consequently, at lower temperatures water scarcely took part in the reaction. Water consumption (25 per cent) can be observed at higher temperatures only. From this the conclusion can be drawn that a considerable decomposition is to be expected only at higher temperatures.

However, steam was necessary even in such cases when it did not take part in the chemical reaction, since in the absence of steam the formation of coke substances in considerable quantities has been observed, in accordance with general working experiences and literature references.

The coke was a mixture of black, lead oxide and lead powder. This coke substance is being formed also in the presence of steam but in considerably smaller quantities.

Experiments have been carried out to investigate the effect of compounds having S content upon the catalyst and the reaction. The experiments have been performed with gasoline containing CS_2 , however, the composition of the gas mixture did not alter considerably. This can be explained by the fact that a poisoning of the catalyst did not arise because, the formed PbS is either removed or regenerated by chemical methods.

On the basis of our experiments the conclusion can be drawn that in the melted-metal reactor used by us the lowest temperature limit of decomposition is $600^\circ C$, and good results can be obtained at $735-750^\circ C$. Our experiments cannot be considered as accomplished.

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ДАННЫЕ К РАЗЛОЖЕНИЮ УГЛЕВОДОРОДА ЖИДКОГО СОСТОЯНИЯ. I

Опыты, полученные при помощи разлагающей металлической плавки

Ю. Шёбел, А. Гилде-Шёбел, Л. Месарош, Т. Селл и И. Галамбос

Реактор металлической плавки оказался пригодным для разложения углеводородов, осуществленного применением водяной пары. При крекировании происходит процесс водяной пары-углеводорода. Реактор можно увеличивать линейно. Плавка не реагирует при отравлении серой. С точки зрения произведения городского газа являются оптимальными 150, длительнее контактное время и питание углеводорода-воды в отношении 1:1.