RESEARCH ON THE BEHAVIOR OF IRON CATALYSTS WHEN OPERATED WITH H_2-RICH SYNTHESIS GAS

I. Introduction

Why are operating temperatures below 200°C. desirable in the middle-pressure synthesis? How can those temperatures be obtained?

II. Tests with Fe Catalysts + 1/4 Percent K_2CO_3

A. Influence of Multi-Stage Operation

More recent experiments in which iron catalysts were used in benzine syntheses have shown that those catalysts will give yields which are very nearly equal to those obtained when using cobalt catalysts. Hydrocarbons obtained with iron catalysts compare favorably also to those obtained by cobalt when one compares their anti-knock properties. The catalysts must be used at temperatures of around 235-260°C., that is, approximately 45-70° higher than cobalt catalysts. When carrying out the middle-pressure synthesis with cobalt catalysts, we have made use of an apparatus which was cooled by steam. It was our desire to use the same set-up for experiments with iron catalysts, without having to make any experimental changes. It would have been advantageous therefore to be able to work at a lower operating temperature. This succeeds when one uses a gas which is richer in hydrogen than a normal gas used along with the iron catalyst.

A time test with mixed gas showed that it is possible to start the synthesis at 210°C. After 15 days of operation and working at 213°C., a yield of 100 g./Nm^3 of ideal gas was still obtained, and the increase in temperature to assure an economical yield was only small. After operating for 180 days, the necessary operating temperature to assure a feasible yield was 235°C.

On the tenth day of the synthesis, 97% of the CO gas was used up, whereas 50% of the initial H_2 constituent remained unconverted. In order to keep the yields up, it was necessary to operate in two stages, and the gas leaving the first stage and entering the second stage had to be replenished with sufficient CO to bring its final composition up to its original value. Before replenishing the gas however for other reasons, it was desired to see what would happen if the gas issuing from stage one was conducted into stage two.

It may be seen that thus it was possible after 70 days of operation to obtain a yield of 157 g./Nm^3 of ideal gas when operating in two stages.

In order to lower the temperatures still more, experiments were carried out in several (4) stages. A gas of composition $CO:H_2 = 1:4$ was used.

In Table II, the results of such a run may be observed. For the first 44 days, the second stage was operated with an initial gas having the composition of the end gas from stage #1, including the gasol hydrocarbons. After the 44th day, the second stage was operated with a gas having been replenished with CO; however, the gasol had been removed. The third and fourth stages were operated with a gas as was obtained from the previous stages and the gasol was left in.

We were able to demonstrate that iron catalysts may be used at temperatures below 200°C., giving economical yields and producing only little CO_2. Generally, it was observed that at the lower temperatures, more water formed than CO_2. The CO consumption is satisfactory, and after the third stage, approximately 90% has been used up. The fourth stage was operated at 170°C., and after 20 days of operation, it was still not necessary to raise the temperature. The CO conversion amounted to 54%.

The yields of stages one and two, were tabulated and referred to 1 N_m^3 of initial gas as fed to the first stage (~~Illegible~~). It was found that after the second stage, 106 g. of hydrocarbons/N_m^3 of ideal gas were obtained. It was furthermore discovered that the gasol in the gas passing over the catalyst in stages 3 and 4 was converted into higher hydrocarbons and no longer could be quantitatively determined as gasol.

Average analysis of exit gas from Stage 1.

CO_2	4.3%
sKW	1.1
CO	7.4
H_2	76.4
KW	3.8
N_2	7.0

On adding 11.7% CO to this gas, one obtains the following gas:

CO_2	3.9%
sKW	1.0
CO	17.1
H_2	68.4
KW	3.4
N_2	6.2

If the second gas has to be compressed into a 40-liter bomb up to a pressure of 160 atmospheres, one requires:

CO_2	6.3%
sKW	1.6
CO	27.3
H_2	109.3
KW	5.5
N_2	10.0

Rheinpreussen-Gasol was available with 32% sKW and 68% KW; therefore only 1.6 atm. sKW had to be added. At the same time, 3.4 atm. KW were compressed into the bomb; however, since 5.5 atm. KW were required, it was necessary to add an additional 2.1 atm. of CH_4. The mixing of the gases was easily accomplished therefore in this manner.

In order to refer the individual yields of the 4 stages to one cubic meter of the original starting gas, it is permissible to work in the individual stages with gases containing gasol. During those experiments, however, the conditions were kept as nearly as possible to actual conditions because it appeared undesirable from the point of view of experience that the gasol of the end-gas should be removed after each stage. The yield determinations of the third and fourth stages show, however, that it is possible to obtain economic quantities of benzine when using iron catalysts (IV).

B. Recycling Experiment

Recycling in general gives similar results to those obtained when working in various stages. Therefore, a recycling experiment was undertaken with a furnace containing 18 reaction tubes and filled with 180 g. of catalyst.

The activity of the catalyst was checked with a CO-rich gas at 180°C., and then operation was started with a gas containing 1CO + 4H_2. The operating temperature was 180°C. The conversion of CO was checked for both recycling as well as one single passage through the tubes. The work was carried out with 24 to 30 liters of end-gas, and approximately 100 liters were circulated. Consequently, during the recirculation, a 3 to 4 times higher flow velocity was obtained in the reaction furnace.

	183°		188°		203°	
	Circulated	Not circulated	Circulated	Not circulated	Circulated	Not circulated
Contraction	26%	27%	33.5%	28%	31.5%	21.4%
C-balance	42.5 g./Nm3	32.5 g./Nm3	31.2 g./Nm3	30.6 g./Nm3	31.2 g./Nm3	24.7 g./Nm3
CO conversion	49%	47.5%	61%	60%	61.5%	52%

The preceding table shows contractions, carbon balance, and CO conversion at three different temperatures. From this experiment, the A.K. benzine was removed at 193°C. (without recirculation), and a distillation was carried through of the constituents boiling at 200°C. The boiling point indicated approximately normal pentane, normal hexane, normal heptane, and normal octane. A yield determination for the experiments of the 18-tube furnace at 193°C, and 30 liters of end-gas per hour showed 41.5 g./Nm3 of ideal gas. This yield was obtained without recycling of the end-gas. No comparative yield was obtained in the recycling experiment because the recycling pump failed to operate after some time.

C. Flow Experiment

The influence of the flow velocity was studied for the same catalyst at different temperatures (10 g. of iron or 16 g. of iron catalyst were charged into the furnace). The following table shows the end-gas quantities, the total gas quantity converted, and the converted CO per hour at various temperatures.

Temperature	Liters end-gas per hr.	Percent contraction	Liters A.C. per hr.	Converted gas quantity per hr.	CO converted per hr.	Percent CO converted
180°	2	37	3.20	1,200 l	0,456 l	80
	4	20	5.00	1,000 l	0,390 l	44
	8	17	9.65	1,650 l	0,660 l	39
190°	2	28	2.78	0,780 l	0,430 l	69
	4	24	5.26	1,260 l	0,544 l	56
	8	14	9.30	1,300 l	0,600 l	33
200°	2	35	3.08	1,080 l	0,531 l	90
	4	27	5.48	1,480 l	0,636 l	61
	8	20	10.00	2,000 l	0,880 l	44

From the tabulation, it is observed how for every temperature the contraction and the CO conversion reduced (about 50%) as the end-gas quantity increases from 2 to 8 liters per hour. Nevertheless, the total quantity of gas and the total quantity of CO converted increases steadily, so, for instance, at 200°C., approximately twice as much gas is converted for 8 liters of end-gas than for 2 liters of end-gas. The yield at 190°C. for 8 liters of end-gas was 34.4 g. of hydrocarbons per normal cubic meter of ideal gas.

D. The Influence of Different Modes of Catalyst Induction Upon the Operation with Hydrogen-Rich Starting Gas

The catalysts have been pretreated in the already well-known manner. We either worked with 4 liters of pure CO (per 10 g. of iron) for 25 hours (100 liters altogether) at 325°C. and 1/10 atm.; or we operated for 2-1/2 hours with 40 liters of CO per hour per 10 grams of iron (100 liters altogether) at 325°C. and 1/10 atm.

In order to investigate the influence of different pretreatments of the catalyst upon operation with hydrogen-rich gas, the first thing we did was that we treated a catalyst according to the earlier methods long enough with mixed gas at 220°C.-255°C. and atmospheric pressure until it gave a contraction of 30% under the same conditions (4 liters per 10 g. of iron per hour). Then we increased the pressure to 15 atm. and a gas of $1CO + 4H_2$ was used at 180°C. and 2 liters per hour of end-gas. It was found that the yield even after a temperature of 200°C. was reached after 6 days of operation, was not as high as the yield when the catalyst was pre-treated under reduced pressure.

	Temperature	Percent Contraction	CO conversion, percent	Days of operation
After pretreatment with mixed gas	181°	12	20	1
	189	12	25	5
	196	22	37	6
	200	20	44	7
	199	20	46	11
	200	20	32	17
	199	20	34	20
	199	17	31	21
After pretreatment in vacuum with pure CO	180	30	71	1
	181	24	60	5
	180	24	66	8
	180	21	58.5	10
	179	16.5	38.5	18
	187	23	48.5	26
	190	34	52	30
	190	23	50	43

When the two methods of pretreatment are compared with each other, it may be noticed that the vacuum treatment has the advantage. With the catalyst having been subjected to the vacuum treatment, the temperature had to be raised to 190°C. only after operating for as long as 30 days. Also, the time of operation, the amount of carbon monoxide converted was higher than in the case of the catalyst pretreated under ordinary pressures. Since in both cases, the same catalyst was

used (78), it is out of the question that the differences in yields could be explained with a loss of activity of the catalyst. An experiment was carried out with a catalyst pretreated in vacuum and operated under normal pressure with a hydrogen-rich gas (1:4). The results are tabulated in the next table and compared to those of the normal pretreated catalyst of the same constituents.

Pretreated 1:4				Not pretreated			
Temperature	Contraction	CO conversion	No. of days	Temperature	Contraction	CO conversion	No. of days
181	4	—	1	180	6	—	1
185	7	—	2	180	5	—	2
195	6	18	3	187	5	—	5
219	10	21	5	200	5	—	7
240	12.5	47	10	210	7	12	8
240	15	51	11	210	7	23	9
240	19	45	15	209	6	20	13
				230	16	40	15

It was not possible to obtain any appreciable amounts of hydrocarbons below 200°C. When working at 240°C. or above, the conversions became normal. Approximately the same results were obtained in both cases when a hydrogen-rich gas was used under normal pressure and low temperatures.

Another experiment was carried out with the same catalyst. However, it was pretreated. The operation was carried through at 15 atm. with hydrogen-rich starting gas (1:4). The operating temperature was kept at 190°C. at first; however, the CO conversion under those conditions was only 10%. When the temperature was raised to 235°C., the contraction increased to 15%, and the CO conversion went up to 38%.

E. Influence of Operating Pressure ~~Series~~

The influence of operating pressure upon the middle-pressure synthesis using iron catalysts was investigated at 0, 1.5, 3.5, 7.5, 15, and 30 atms. The following table shows the effect of the various pressures. In all cases, the catalyst used was the same as described before, and was pretreated prior to all experiments in a vacuum by using pure CO.

0 atm. (see above table)				1.5 atm.				3.5 atm.			
Temp.	Contraction	CO conversion	No. of days	Temp.	Contraction	CO conversion	No. of days	Temp.	Contraction	Co conversion	No. of days
181	4	—	1	180	9	29	2	181	33	60	2
185	7	—	2	180	17	43	7	180	37	91	7
195	6	18	3	180	15	27	10	181	20	60	10
219	10	21	5	189	26	58	34	180	20	57	16
240	12.5	47.5	10	190	22	52	27	180	14	48	23
240	15	51	11	190	8	23	37	180	23	42	32
240	19	45	15	190	6	31	39	189	31	59	37
								190	26	58	47

Temp.	Contraction	% conversion	No. of days	Temp.	Contraction	% conversion	No. of days	Temp.	Contraction	% conversion	No. of days
181	34	52	2	180	30	71	1	178	33	[illegible]	[illegible]
180	38	82	7	181	24	60	5	180	40	[illegible]	[illegible]
180	25	70	10	180	24	66	8	175	32	[illegible]	[illegible]
180	30	71	15	180	21	58	10	175	30	[illegible]	[illegible]
181	26	64	22	179	17	38	18	180	25	[illegible]	[illegible]
182	32	68	32	179	19	33	24	179	19	[illegible]	[illegible]
180	27	55	36	187	23	48	26	190	23	[illegible]	[illegible]
180	21	52	49	190	34	62	30	179	20	[illegible]	[illegible]
				190	23	50	43	180	21	[illegible]	[illegible]
								190	37	[illegible]	[illegible]
								183	21	[illegible]	[illegible]

The experiments at 0 atm. and 1.5 atm. are unsatisfactory at low temperatures. The run at 3.5 atm. showed a 40% conversion of CO after a month of operation at 180°C. The experiment at 7.5 atm. showed the best results. After 50 days of operation at 180°C., the conversion had not decreased below 50%, and up to this time only a slow decrease in activity of the catalyst was observed. The yield determination between the 34th and 38th day of operation still showed 40.5 g. of total hydrocarbons per m³ of ideal gas. When working under 15 atm., it was necessary to raise the temperature from 180 to 190°C. after 25 days of operation. A yield determination between the 16th and 20th days of operation showed 34.5 g. of total hydrocarbons per m³ of ideal gas. The 30 atm. run showed an initial activity corresponding to 100% CO conversion. In order to avoid over-heating of the catalyst, the temperature had to be dropped to 175°C. However, it could be raised again to 180°C. on the 6th day. However, on the 20th day of operation, the conversion had dropped to 62%, and a temperature increase to 190°C. was unavoidable. However, this increase did not help indefinitely. The yield determination between the 9th and 13th days of operation showed 45 g. of total hydrocarbons per m³ of ideal gas. From all of these experiments, it may be observed that the most favorable pressure is 7.5 atm. when using a hydrogen-rich gas of composition 1CO + 4H₂. It is probable that the best CO conversion occurs somewhere around 10 atm. (see tabulation 5)

F. Tests with 1CO + 6H₂ Gas Mixture.

In order to lower the working temperature some more, when working with iron catalysts, an experiment was carried out with an initial gas of composition 1CO + 6H₂ (same catalyst and same pretreatment as before). The experiment was started at 15 atm. and 160°C.

Temperature	Contraction	CO conversion	No. of days
160°	33%	70%	3
159	26	62	3
160	29	62	4
160	32	65	3
160	24	55	17
160	22	60	10 ?
160	20	52	20
160	20	45	21

The carbon balance on the 13th to 21st days of operation showed 23 g. of condensable hydrocarbons per m³ of gas. It was remarkable how little CO_2 was formed.

B. Normal Pressure Experiments

Another series of experiments was run with Fe and Cu catalysts and normal pressures and various starting gases containing different proportions of hydrogen and carbon monoxide. Both
Ferri- and Ferro-copper catalysts were used at normal temperature, and were tested for their activity by using mixed gas;at correspondingly lower temperatures.

Ferri - Cu Catalyst

1 : 2				1 : 2 (Parallel Test)			
Temperature	Percent Contraction	Percent CO con-version	Days	Temperature	Percent Contraction	Percent CO con-version	Days
235°	21	--	2	235°	22	--	2
236	32	--	3	235	25	--	4
229	26	80	4	233	27	--	5
229	28	70	8	231	25	--	7
230	22	--	9	245	30	--	8
231	18	--	13				
245	33	--	14				
1 : 4				1 : 6			
201	13	24	2	200	6	--	2
201	18	(%0)	3	200	5	--	4
200	14	24	4	205	6	--	5
205	10	27	6	207	3	--	8
210	9	--	8				

Ferro - Cu Catalyst

1 : 2				1 : 2 (Parallel Test)			
236	34	90	2	231	31	--	2
232	30	--	3	228	30	90	3
232	32	90	4	227	34	--	7
229	28	90	8	229	30	90	8
231	31	90	10	230	33	90	10
238	25	--	19	230	34	--	11
1 : 4				1 : 6			
201	4	--	2	205	3	--	2
210	12	30	3	209	10	28	3
213	11	59	7	210	13	40	4
215	13	--	10	210	13	43	8
				215	17	70	10

The higher activity of the Ferro-Copper catalysts is especially apparent when operating with gas at temperatures of above 230°C. But when working with the hydrogen rich gases at around 215°C., this higher activity is scarcely noticeable.

When the experiments are compared with those employing a copper-free not pretreated catalyst, no important improvement can be noticed over a copper containing catalyst for the temperature range of 200-210°C.

Only approximately xunreadablex of the end gas consisted of CO_2.

This experiment a___ proves that benzine may be produced at lower temperatures when using iron catalysts than the temperatures of the middle-pressure synthesis using cobalt.

Concerning the products of this reaction, it may be said that the paraffins obtained were of remarkably light color when using a hydrogen-rich gas. When a CO-rich gas was used, the products of the iron and middle-pressure synthesis were brown. The results have been given already on the distillation analyses of the fractions boiling below 200°C. (page 3).

One Percent Alkali Experiment

An experiment was carried out at 15 atm. And 180°C., with the catalyst containing one percent potassium carbonate. The gas used consisted of $1CO = 4H_2$. It was found that the activity of this catalyst was considerable lower. Fe obtained yellow oil without solid paraffin.

III. Tests with Iron-Copper Catalysts.

Earlier experiments show that small additions of copper improved the activity of iron catalysts. In order to investigate this effect with a hydrogen-rich gas, Fe-Cu Catalysts were compounded. The catalysts used contained 5 parts of Fe and one part of Cu. The copper was co-precipitated with the iron. After the precipitation, the precipitate was made alkaline with ¼% of potassium carbonate.

A. Influence of Pressure.

The Ferri-Cu Catalyst (5:1) was pretreated in a vacuum and was used for three experiments. One experiment was run at 0 atm., another at 1.5 atm., and a third at 15 atm. Pressure, using a hydrogen-rich starting gas. The following tabulation shows the results of the experiments.

0 atm.				1.5 atm.				15 atm.			
Temp	Con-trac-tion	No. of days	CO con-version	Temp	Con-trac-tion	No. of days	CO con-version	Temp	Con-trac-tion	No. of days	CO con-version
189°	6%	1	--	180°	--	2	--	176°	24%	1	59%
185	5	5	6	180	14	8	20	182	23	6	46
215	25	16	24	180	13	10	24	181	25	10	48
216	16	19	23	190	24	13	45	180	26	19	56
225	22	31	20	190	27	16	52	185	40	22	64
				193	13	29	42	185	32	25	59
								188	22	33	48

A comparison with the corresponding experiments carried out with a copper-free catalyst shows that for 0 and 1.5 atm., no improvements were observed. At 15 atm., it appears that a small increase in catalyst activity was noticed (see also tabulation 6).

APPENDIX

TOM Reel 101 Doc. PG-21559-WID

TOM Reel 101 Doc. PG-21574-NID