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

INTRODUCTION

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

TESTS WITH IRON CATALYSTS CONTAINING 1/4 PERCENT K_2CO_3, USING H_2-RICH GAS

Influence of Multistage Operation.

More recent experiments in which iron catalysts were used in the benzine synthesis have shown that those catalysts will give yields nearly equal to those obtained with cobalt catalysts. Hydrocarbons obtained with iron catalysts compare favorably in their antiknock properties with those obtained from cobalt. The catalysts must be used at temperatures of around 235° to 260°C., that is, approximately 45° to 70° higher than cobalt catalysts. When carrying out the middle-pressure synthesis with cobalt catalysts, we used an apparatus cooled by steam. It was our desire to use the same equipment for experiments with iron catalysts. It would have been advantageous, therefore, to be able to work at a lower operating temperature. This is possible when one used a synthesis gas richer in hydrogen than a normal gas used with the iron catalysts.

A durability test with mixed gas showed that it is possible to start the synthesis at 210°C. After 15 days of operation at 213°C., a yield of 100 grams per normal cubic meter of ideal gas was still obtained, and the increase in temperature to assure an economical yield was small. After operating for 180 days, the necessary operating temperature to assure a good yield was 235°C.

On the tenth day of the synthesis, 97 percent of the CO gas was used up, whereas 50 percent of the initial H_2 constituent remained unconverted. To maintain yields, it was necessary to operate in two stages, and the gas leaving the first stage and entering the second stage was 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 determine the effect if the gas issuing from stage 1 was conducted into stage 2.

It may be seen that thus it was possible after 70 days of operation to obtain a yield of 157 grams per normal cubic meter of ideal gas when operating in two stages.

In order to lower the temperatures further, experiments were carried out in four stages. A gas of composition $CO:H_2 = 1:4$ was used. A run was made in which the following conditions prevailed. For the first 44 days, the second stage was operated with the gas issuing from stage 1, excluding the gasol hydrocarbons. The third and fourth stages were operated with a gas obtained from the previous stages, and the gasol was retained.

We demonstrated that iron catalysts at temperatures below 200°C. can give economical yields and produce little CO_2. Generally, it was observed that at the lower temperatures, more water formed than CO_2. The CO consumption was satisfactory, and after the third stage, approximately 90 percent had been used up. The fourth stage was operated at 170°C., and after 20 days of operations, it was still not necessary to raise the temperature. The CO conversion amounted to 64 percent.

The yields of stages 1 and 2 were tabulated and referred to 1 normal cubic meter of initial gas as fed to the first stage. It was found that after the second stage, 106 grams of hydrocarbons per normal cubic meter 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, percent.

CO_2	4.3
Olefins	1.1
CO	7.4
H_2	76.4
Hydrocarbons	3.8
N_2	7.0

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

CO_2	3.9
Olefins	1.0
CO	17.1
H_2	68.4
Hydrocarbons	3.4
N_2	6.2

If the second gas is compressed into a 40-liter bomb up at a pressure of 160 atmospheres, one requires (in percent):

CO_2	6.3
Olefins	1.6
CO	27.3
H_2	109.3
Hydrocarbons	5.5
N_2	10.0

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

In order to refer the individual yields of the four stages to 1 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 to remove the gasol from the end gas after each stage. The yield determinations of the third and fourth stages show that it is possible to obtain high yields of gasoline when iron catalysts are used.

Recycling Experiment.

Recycling in general gives results similar to those obtained when in multistage operation. Therefore, a recycling experiment was undertaken with a furnace containing 18 reaction tubes and filled with 180 grams 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 multi- as well as 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 three to four times higher flow velocity was obtained in the reaction furnace.

	183°		188°		203°	
	Circulated	Not circulated	Circulated	Not circulated	Circulated	Not circulated
Contraction, percent	26	27	33.5	28	31.5	21.4
C-balance, grams per normal cubic meter	42.5	32.5	31.2	30.6	31.2	24.7
CO conversion, percent	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. Boiling point determinations indicated the presence of 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 grams per normal cubic meter of ideal gas. This yield was obtained without recycling of the end gas. No comparative yield was obtained in the recylcing experiment because the recycling pump failed during operation.

Flow Experiment.

The influence of space velocity was studied for the same catalyst at different temperatures (10 grams of iron or 16 grams 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, °C.	End-gas liters per hr.	Contraction, percent	In-gas liters per hr.	Quantity of converted gas liters per hr.	CO converted liters per hr.	CO converted, percent
180	2	37	3.20	1.200	0.456	80
	4	20	5.00	1.000	0.390	44
	8	17	9.65	1.650	0.660	39
190	2	28	2.78	0.780	0.430	69
	4	24	5.26	1.260	0.544	56
	8	14	9.30	1.300	0.600	33
200	2	35	3.08	1.080	0.531	90
	4	27	5.48	1.480	0.635	61
	8	20	10.00	2.000	0.830	44

From the tabulation, it is observed how for every temperature the contraction and the CO conversion reduced (about 50 percent) 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; for instance, at 200°C., approximately twice as much gas is converted for 8 liters of end gas as for 2 liters of end gas. The yield at 190°C. for 8 liters of end gas/34.4 grams of hydrocarbons per normal cubic meter of ideal gas. was

Influence of Different Modes of Catalyst Induction Upon Operation With Hydrogen-Rich Starting Gas

The catalysts were pretreated with 4 liters of pure CO (per 10 grams of iron) for 25 hours (100 liters total) at 325°C. and 1/10 atmosphere or with 40 liters of CO per hour per 10 grams of iron for 2-1/2 hours (100 liters total) at 325°C. and 1/10 atmosphere.

In order to investigate the influence of different methods of pretreatment of the catalyst upon operation with hydrogen-rich gas, we treated a catalyst, according to the earlier methods, with mixed gas at 220°C. to 255°C. and atmospheric pressure long enough to give a contraction of 30 percent under the same conditions (4 liters per 10 grams of iron per hour). Then we increased the pressure to 15 atmospheres; the gas was a mixture of $1CO + 4H_2$ at 180°C. at a rate of 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 obtained when the catalyst was pretreated under reduced pressure.

	Temperature, °C.	Contraction, percent	CO conversion, percent	Operation, days
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 vacuo 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 is obvious that the reduced pressure treatment is better. When the catalyst has been subjected to the vacuum treatment, the temperature had to be raised to 190°C. after operating 30 days. Also, 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 (Z8), it is obvious that the differences in yields could be attributed to a loss of activity of the catalyst. An experiment was carried out with a catalyst pretreated in vacuo and operated under normal pressure with a hydrogen-rich gas (1:4). The results are tabulated in the next table and compared with those of the normal pretreated catalyst of the same composition.

Pretreated CO:H_2 1:4				Not pretreated			
Temperature, °C.	CO conversion, percent	Contraction, percent	Operation, days	Temperature, °C.	CO conversion, percent	Contraction, percent	Operation, days
181	—	4	1	180	—	6	1
185	—	7	2	187	—	5	2
195	18	6	3	187	—	5	5
219	21	10	5	200	—	5	7
240	47	12.5	10	210	12	7	8
240	51	15	11	210	23	7	9
240	45	19	15	209	20	6	13
				230	40	16	15

It was not possible to obtain any appreciable amounts of hydrocarbons below 200°C. 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 out at 15 atmospheres with H_2-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 percent. When the temperature was raised to 235°C., the contraction increased to 15 percent, and the CO conversion to 38 percent.

Influence of Operating Pressure.

The influence of operating pressure upon the middle-pressure synthesis using iron catalysts was investigated at 1, 1.5, 3.5, 7.5, 15, and 30 atmospheres. 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 before all experiments in vacuo with pure CO.

1 atmosphere (see above table)				1.5 atmospheres				3.5 atmospheres			
Temp., °C.	Contraction, percent	CO conversion, percent	Operation, days	Temp., °C.	Contraction, percent	CO conversion, percent	Operation, days	Temp., °C.	Contraction, percent	CO conversion, percent	Operation, 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	24	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

7.5 atmospheres				15 atmospheres				30 atmospheres			
181	34	52	2	180	30	71	1	180	60	100	2
180	38	82	7	181	24	60	5	180	50	100	3
180	25	70	10	180	24	66	8	175	33	75	4
180	30	71	15	180	21	58	10	178	30	56	5
181	26	64	22	179	17	38	18	180	25	61	6
182	32	68	32	179	19	33	24	179	19	39	10
180	27	55	36	187	23	48	26	180	18	39	13
180	21	52	49	190	34	62	30	179	20	42	19
				190	23	50	43	190	31	53	23
								190	37	65	25
								188	21	41	35

The experiments at 1 atmosphere and 1.5 atmospheres are unsatisfactory at low temperatures. The run at 3.5 atmospheres showed a 40 percent conversion of CO after a month of operation (at 180°C.). The experiment at 7.5 atmospheres showed the best results. After 50 days of operation at 180°C., the conversion had not dropped below 50 percent, and only a slow decrease in activity was observed. The yield between the 34th and 38th day of operation was still 40.5 grams of total hydrocarbons per normal cubic meter of ideal gas. At 15 atmospheres, it was necessary to raise the temperature from 180° to 190°C. after

25 days of operation. The yield between the 16th and 20th days of operation was 34.5 grams of total hydrocarbons per normal cubic meter of ideal gas. The 30-atmosphere run showed an initial activity corresponding to 100 percent CO conversion. To avoid overheating 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. On the 20th day of operation, the conversion had dropped to 42 percent, and a temperature increase to 190°C. was unavoidable. However, this increase did not help indefinitely. The yield between the 9th and 13th days of operation was 45 grams of total hydrocarbons per normal cubic meter of ideal gas. From all of these experiments, it may be observed that the most desirable pressure is 7.5 atmospheres when using a hydrogen-rich gas of composition $1CO + 4H_2$. It is speculated that the best CO conversion occurs somewhere at about 10 atmospheres.

Tests With $1CO + 6H_2$ Gas Mixture.

In order to lower the operating temperature further, when working with iron catalysts, an experiment was carried out with an initial gas of composition $1CO + 6H_2$ (same catalyst and same pretreatment as before). The experiment was started at 15 atmospheres and 160°C.

Temp., °C.	Contraction, percent	CO conversion, percent	Operation, days
160	31	70	2
159	26	62	3
158	29	62	4
160	22	55	8
160	24	55	13
160	22	60	18 ?
160	20	55	20
160	20	45	21

The carbon balance on the 13th to 21st days of operation showed the presence of 23 grams of condensable hydrocarbons per normal cubic meter of gas. It was remarkable how little CO_2 was formed.

Only approximately 0.7 percent of the end gas consisted of CO_2.

This experiment also proves that gasoline may be produced with iron catalysts at temperatures lower than those used with cobalt in the middle-pressure synthesis.

Concerning the products of this reaction, the paraffins obtained were of remarkably light color when a hydrogen-rich gas was used. When a CO-rich gas was used, the products of the iron and middle-pressure syntheses were brown. The results have been given already on the distillation analyses of the fractions boiling below 200°C. (p. 161).

One-Percent Alkali Experiment.

An experiment was carried out at 15 atmospheres and 180°C., with the catalyst containing 1 percent potassium carbonate. The gas used consisted of $1CO + 4H_2$. It was found that the activity of this catalyst was considerably lower. We obtained yellow oil without solid paraffin.

TESTS WITH IRON-COPPER CATALYSTS.

Earlier experiments showed 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 containing 5 parts of Fe and 1 of Cu. The copper was coprecipitated with the iron. After the precipitation, 1/4 percent of potassium carbonate was added.

Influence of Pressure.

The ferric-Cu catalyst (5:1) after pretreatment in vacuo was used for three experiments. One was run at 1 atmosphere, another at 1.5 atmospheres, and a third at 15 atmospheres pressure, using a hydrogen-rich starting gas. The following tabulation shows the results of the experiments.

1 atmosphere				1.5 atmospheres				15 atmospheres			
Temp., °C.	Contraction, per cent	CO conversion, percent	Operation, days.	Temp., °C.	Contraction, per cent	CO conversion, percent	Operation, days	Temp., °C.	Contraction, per cent	CO conversion, percent	Operation, days
189	6	—	1	180	—	—	2	176	24	59	1
185	5	6	5	180	14	20	8	182	23	46	6
215	15	24	16	180	13	24	10	181	25	48	10
216	16	23	19	190	24	45	13	180	26	56	19
225	22	20	31	190	27	52	16	185	40	64	22
				193	13	42	29	185	32	59	25
								188	22	48	33

A comparison with the corresponding experiments with a copper-free catalyst shows that for 1 and 1.5 atmospheres, no improvement was observed. At 15 atmospheres, a slight increase in catalyst activity was noticed.

Normal Pressure Experiments.

Another series of experiments was run with iron and copper catalysts at normal pressures with starting gases containing different proportions of hydrogen and carbon monoxide. Both ferric and ferrous copper catalysts were used at normal temperature, with mixed gas; then catalysts of the same composition were used with hydrogen-rich gas at correspondingly lower temperatures.

The higher activity of the ferrous-copper catalysts is especially apparent with mixed gas at temperatures above 230°C., but with the hydrogen-rich gases at around 200° to 215°C., the activity is not higher.

When these experiments are compared with those employing a copper-free, unpretreated catalyst, no important improvement could be noticed for the temperature range of 200° to 210°C.

Operation, days	Temp., °C.	Contraction, percent	CO conversion, percent	Operation, days	Temp., °C.	Contraction, percent	CO conversion, percent
Ferric copper catalyst							
$CO:H_2$ = 1:2				1:2 (duplicate test)			
2	235	21	—	2	235	22	—
3	236	32	—	4	235	25	—
4	229	26	80	5	233	27	—
8	229	28	70	7	231	25	—
9	230	22	—	8	245	30	—
13	231	18	—				
14	245	33	—				
$CO:H_2$ = 1:4				1:6			
2	201	13	24	2	200	6	—
3	201	18	(0)	4	200	5	—
4	200	14	24	5	205	6	—
6	205	10	27	8	207	3	—
8	210	9	—				
Ferrous copper catalyst							
$CO:H_2$ = 1:2				1:2 (duplicate test)			
2	236	34	90	2	231	31	—
3	232	30	—	3	228	30	90
4	232	32	90	7	227	34	—
8	229	28	90	8	229	30	90
10	231	31	90	10	230	33	90
19	238	25	—	11	230	34	—
$CO:H_2$ = 1:4				1:6			
2	201	4	—	2	205	3	—
3	210	12	30	3	209	10	28
7	213	11	59	4	210	13	40
10	215	13	—	8	210	13	43
				10	215	17	70

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