FURTHER STUDIES OF THE FISCHER-TROPSCH SYNTHESIS USING GAS RECYCLE COOLING (HOT-GAS-RECYCLE PROCESS)

By J. H. Field, D. Bienstock, A. J. Forney, and R. J. Demski

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Ьу

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SUMMARY

Synthesis of hydrocarbons by the Fischer-Tropsch reaction in a hot-gasrecycle system was demonstrated to be technically feasible. This project was undertaken, by the Bureau of Mines, to determine if the system was operable and to ascertain the optimum conditions for the production of gasoline.

Carbon steel turnings packed with a void volume from 88 to 90 pct. were satisfactory catalysts, but steel catalysts with greater void volume, either turnings or steel wool, were not as active.

Good temperature control with a pressure drop of less than 0.5 pounds per square inch (p.s.i.) per foot of catalyst bed of turnings was obtained by operating with a recycle to fresh feed ratio of 20 and by splitting the total gas flow and injecting portions into the reactor at different entry ports.

At an hourly space velocity of 1,000, 90 pct. of the feed gas was converted at 300° to 320° C. At a space velocity of 1,500, 88 pct. was converted The proportion of gasoline in the hydrocarbon product ranged from 55 to 66 pct. The finished gasoline with 3 cc. of tetraethyl lead had research octane ratings from 90 to 96. Synthesis of gasoline in a hot-gas-recycle process is preferable to processes using oil as coolant. At the higher temperatures possible in the hot-gas system, a larger percentage of the hydrocarbon product is gasoline.

INTRODUCTION

The Bureau's program on the synthesis of liquid fuels from coal includes the development and evaluation of reactor systems for the catalytic

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hydrogenation of carbon monoxide. Methods for conducting the synthesis differ principally in the technique of removing the exothermic heat of reaction and in the type and form of catalyst. Heat is removed directly by a cooling medium contacting the catalyst surface in the oil circulation, slurry, and hot-gas-recycle processes, and indirectly in fluidized bed and fixed bed systems.

In the hot-gas recycle process the exothermic heat of reaction (about 70 B.t.u./cu.ft. of synthesis gas converted) is absorbed by the sensible heating of large volumes of recycle gas circulating through the reactor in direct contact with the catalyst. The heat absorbed by the recycle gas is then removed externally in a waste heat beiler by generating steam. Because of the large volumes of gas and the high cost of compression, it is necessary to have a low pressure drop through the catalyst bed. The development by the Bureau of an active lathe turning catalyst having a considerably lower resistance to gas flow and better heat-transfer characteristics than granular catalysts has overcome the major difficulties experienced by the Germans in 1938.

Assuming a constant specific heat of the gas and a constant rate of heat transfer from the catalyst to the gas, the amount of recycle required depends on the temperature increase which can be tolerated across the catalyst bed. An excessive temperature rise would inactivate the catalyst and promote the deposition of carbon. A temperature rise of 40° gave no operating difficulties in the present studies; this is 4 times the temperature differential that could be tolerated in the early German studies.

The purpose of these experiments was to demonstrate the feasibility of the hot-gas-recycle process with an active catalyst that offers a low resistance to gas flow and to determine the operating variables which affect the production and quality of gasoline and the life and activity of the catalyst. A previous report¹² discussed the use of a simulated hot-gas-recycle system in

Schlesinger, M. D., Crowell, J. H., Leva, M., and Storch, H. H., Fischer-Tropsch Synthesis in Slurry Phase: Ind. Eng. Chem., vol. 43, 1951, pp. 1474-1479.

⁷Bienstock, D., Jimeson, R. M., Field, J. H., and Benson, H. E., The Fischer-Tropsch Synthesis Using Gas Recycle Cooling (Simulated Hot-Gas-Recycle Process): Bureau of Mines Rept. of Investigations 5655, 1960, 25 pp.

⁸Demeter, J. J., and Schlesinger, M. D., Fischer-Tropsch Synthesis in a Fluidized-Catalyst Reactor with a Nitrided, Fused-Iron Catalyst: Bureau of Mines Rept. of Investigations 5456, 1959, 16 pp.

Storch, H. H., Golumbic, N., and Anderson, R. B., The Fischer-Tropsch and Related Syntheses: John Wiley and Sons, Inc., New York, N.Y., 1951, 610 pp.

10Work cited in footnote 9.

llwork cited in footnote 9.

12Work cited in footnote 7.



Benson, H. E., Field, J. H., Bienstock, D., Nagel, R. R., Brunn, L. W.,

Hawk, C. O., Crowell, J. H., and Storch, H. H., Development of the Fischer
Tropsch Oil-Recycle Process: Bureau of Mines Bull. 568, 1957, 72 pp.

which the recycle gas was cooled, compressed, and reheated to reactor temperature. Cooling the recycle gas below 25° C. results in condensing and removing from the system water and higher-boiling hydrocarbons. This simulated system was used until a compressor capable of circulating hot gases was installed in the pilot plant.

EXPERIMENTAL PROCEDURES

Raw Materials

Synthesis Gas

Synthesis gas was produced for the hot-gas-recycle pilot plant by reforming natural gas with steam and carbon dioxide over a nickel catalyst at atmospheric pressure in a small commercial unit. Hydrogen-to-carbon monoxide ratios were varied from 1.0 to 3.0. Impurities in the synthesis gas, methane, carbon dioxide and nitrogen amounted to less than 1 pct. The sulfur content was kept below 0.1 grain (gr.) per 100 cu.ft. by passing the gas through activated carbon. Usually the sulfur content was less than 0.02 gr. per 100 cu.ft.

Catalyst

Steel lathe turnings and steel wool were catalysts in these experiments. The turnings, made of 1018 carbon steel, were cut on a lathe, and the cutting depth, angle, and speed could be adjusted to produce turnings with void volumes from 88 to 96 pct. No. 6 commercial grade steel wool was used in two experiments and was packed in the reactor to a void volume of 97 pct.

Apparatus and Method of Operation

The pilot plant consisted of a reactor, recycle compressor, carbon dioxide scrubbing system, product recovery system, and heat exchangers. The catalyst was oxidized in a separate unit. A simplified flowsheet of the hot-gas-recycle process is shown in figure 1. A more detailed view of the reactor indicating gas ports, pressure taps, catalyst sampler, and thermocouples is illustrated in figure 2. The reactor is a 3-in. schedule 80 pipe made of ASTM type A-106 steel, grade B. A maximum catalyst bed height of 10 ft. could be used, but all of the experiments discussed in this report were made with a 6-ft. bed equal to a volume of 0.275 cu.ft.

As shown in figure 1, the total feed gas, consisting of fresh and recycle gases, enters the top of the reactor and flows downward through the catalyst bed at a superficial linear velocity of about 4 to 5 ft./sec. The gas leaving the reactor enters a gas-to-gas heat exchanger where it is cooled to 200°-250° C. The effluent gas stream from the reactor is divided in the following manner: The product gas stream is cooled, metered, and sampled; the remainder is returned to the system by the hot-gas-recycle compressor. Five to 15 pct. of the hot recycle gas is cooled to condense the water vapor and oil and treated with monoethanolamine to absorb the carbon dioxide. Thus the carbon dioxide

¹³Work cited in footnote 7, p. 2.



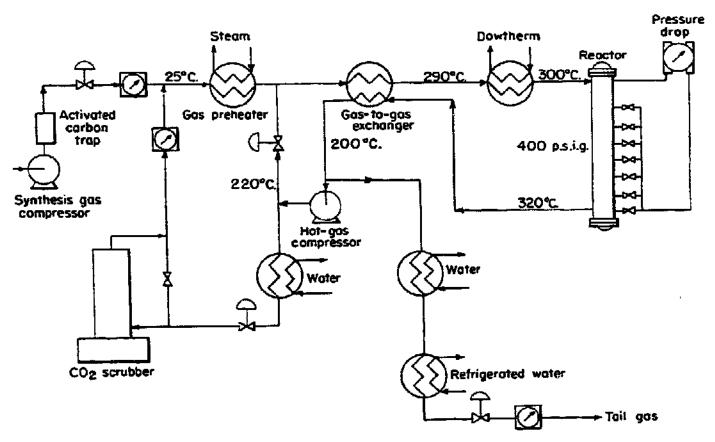


FIGURE 1. - Schematic Flowsheet of Hot-Gas-Recycle Process.

and water vapor content of the recycle stream are both maintained below 10 pcr. This cold recycle then recombines with the remainder of the hot recycle gas and with the fresh feed gas, and flows to the reactor through the gas-to-gas heat exchanger and a Dowtherm-jacketed¹⁴ gas heater. The recycle booster compressor is shown in detail in figure 3; it is a single-cylinder, double-acting reciprocating type. Figure 4 shows the compressor. The gas is compressed from 400 to 500 pounds per square inch gage (p.s.i.g.), and can be operated at temperatures as high as 325° C. The capacity at these conditions is 27,000 standard cubic feet per hour (std. cu.ft./hr.).

Carbon dioxide is removed from the cold recycle gas by a 20-pct. monoethanolamine solution that is fed into the top of the absorber through a distributor and flows countercurrent to the gas. The absorber column is 6 in. in diameter, packed to a height of 8 ft. with 3/4-in. ceramic Raschig rings. The stripper column is also 6 in. in diameter, containing 6 ft. of the same type packing. Any part of the cooled recycle gas could be sent to the absorber. This method of operation permitted the water vapor content and the carbon dioxide content in the recycle gas to be controlled independently.

¹⁴Reference to brand names is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.



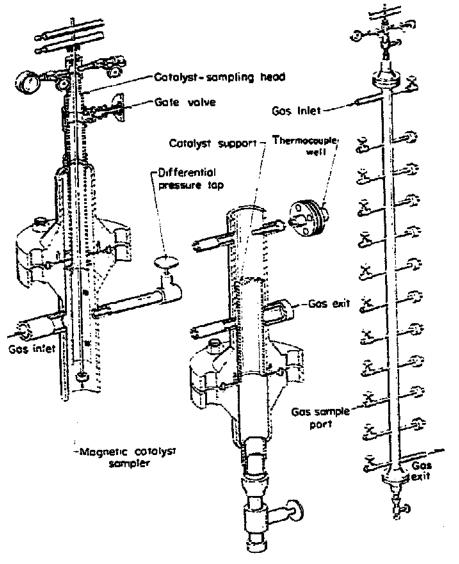


FIGURE 2. - Hot-Gas-Recycle Reactor.

Figure 5 shows schematically the unit used for oxidizing massive from catalysts such as turnings and steel wool. The oxidizer is a 6-in. pipe made of 304-stainless steel. capacity is 0.3 cu.ft. Distilled water is converted to steam which is then superheated by passing through a tube coil wound around the oxidizer. The steam reacts with the iron to form Fe3 O4 and hydrogen. The unreacted steam is condensed and the hydrogen flows through a drying tower and is metered. yield of hydrogen indicates the degree of oxidation.

Operations

Oxidation

Oxidation followed by reduction of the turnings makes the steel porous and increases the surface area, resulting in a catalytically active material. The oxidations were made at 600° C. and atmospheric pressure using a steam flow of about 400 hourly space

velocity. The steel was oxidized until 20 pct. of the iron was converted to Fe₃O₄. The degree of oxidation is checked by comparing the weight gain of the catalyst with the amount of hydrogen evolved. Oxidation in this manner produces a layer of iron oxide with the bulk of the steel in the interior unoxidized.

Impregnation

Storch has shown that alkali impregnation of massive iron catalysts shifts the product distribution toward the higher boiling hydrocarbons and minimizes the yield of gaseous hydrocarbons. The catalysts used in these experiments were impregnated with an aqueous solution of potassium carbonate, and then dried. The strength of the solution and length of time the material

¹⁵Work cited in footnote 9, p. 2.



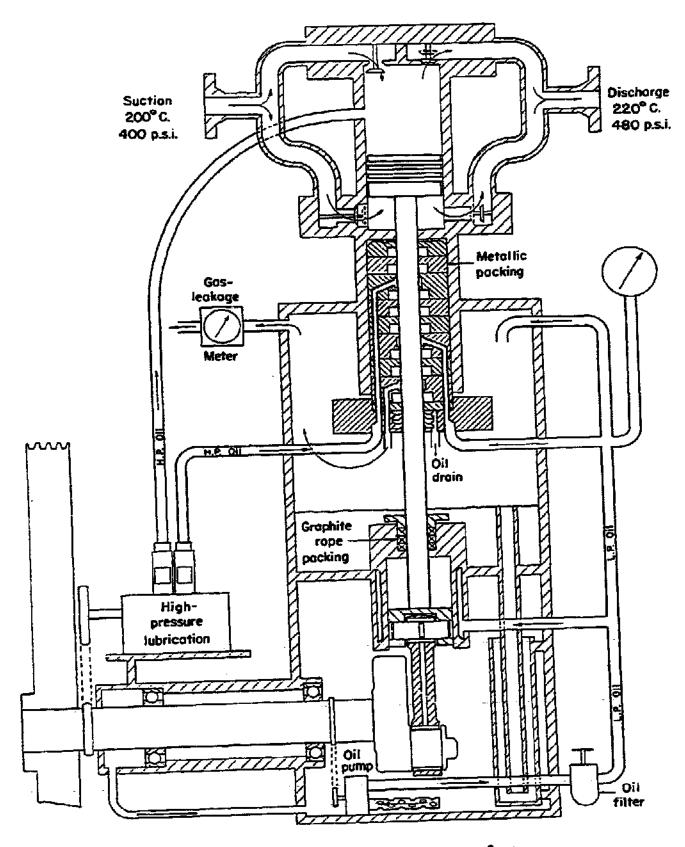


FIGURE 3. - Hot-Gas-Recycle Compressor System.



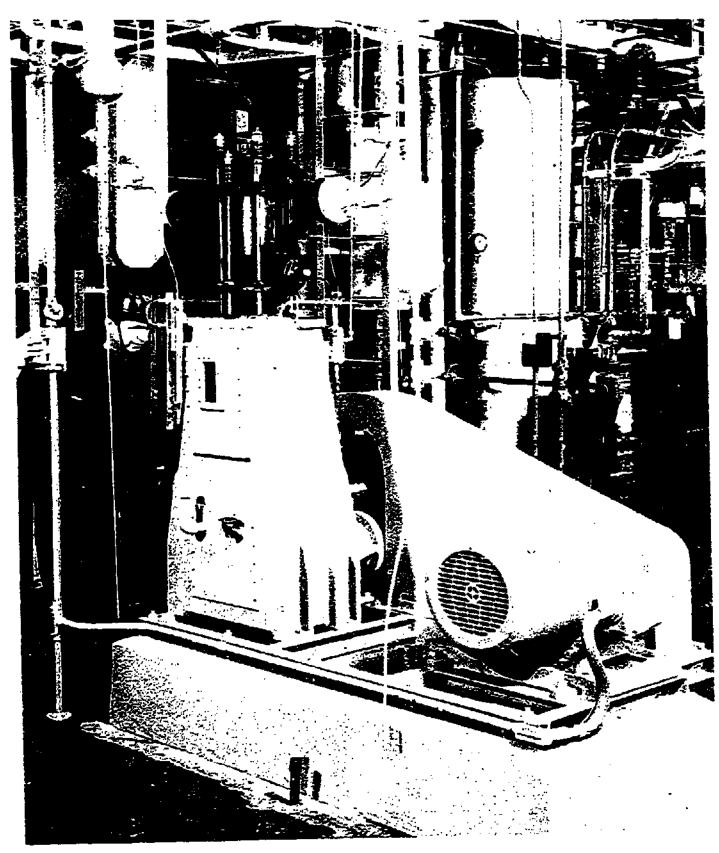


FIGURE 4. - Hot-Gas-Recycle Compressor.



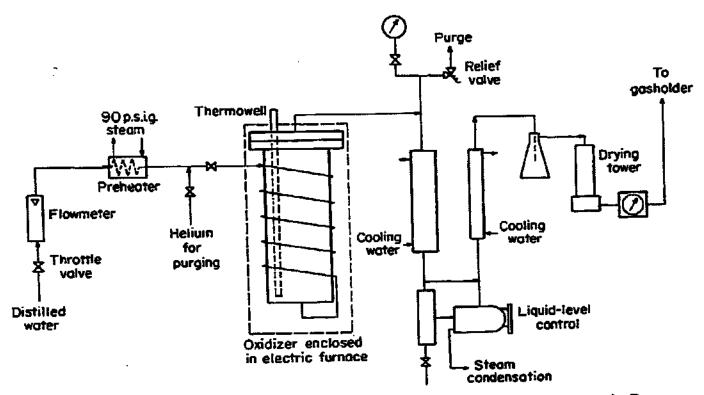


FIGURE 5. - Oxidation Unit for Preparing the Steel Catalyst for the Hot-Gas-Recycle Process.

was immersed in the solution determined the potassium content of the catalyst. The potassium content of catalysts, expressed as potassium oxide, varied from 0.04 to 0.36 pct.

Reduction

The catalysts were reduced after oxidation and impregnation. The reductions were conducted in the reactor of the pilot plant. Usual conditions were: Thirty cubic feet per hour of fresh hydrogen, 2,000 cu.ft./hr of recycle hydrogen, 100 p.s.i.g. reactor pressure, and 400° C. average temperature. The recycle stream was cooled to remove water and then reheated. The temperature was limited by the heat transfer fluid (dowtherm) used in the preheater. All reductions were 40 to 60 hours in duration. The phase present on the surface of the catalyst after reduction was shown by X-ray diffraction to be predominantly alpha-Fe.

Synthesis

After reduction the catalysts were usually inducted in the reactor to bring the system to operating conditions. Induction was accomplished by operating 10 days at the following conditions: An hourly space velocity of 200 to 250, an average bed temperature of 260°-270° C., a reactor pressure of 400 p.s.i.g., and a hot-gas-recycle rate sufficient to maintain the temperature differential over the catalyst bed at 10° C. The feed gas had a



hydrogen-carbon monoxide ratio of 1.0. After the induction period, the hydrogen-carbon monoxide ratio of the fresh gas was changed to 1.3-1.5, the hourly space velocity was increased, while maintaining a CO₂-free contraction of 65 to 70 pct., and the average bed temperature was raised to 300°-320° C. The recycle rate was adjusted to give a differential across the bed of 20° C. The cold recycle stream was generally 5 pct. of the total recycle. Samples of gaseous and liquid products were taken at periodic intervals after steady-state conditions were obtained. Weight balances were also made during these periods.

Catalyst Analysis

Catalyst samples were analyzed by X-ray diffraction for the determination of the solid phases present. These samples were taken from the top of the catalyst bed during synthesis by using the sampler shown in figure 2. The apparatus was attached to the top of the reactor and the magnetic sampler was lowered to recover sufficient turnings for X-ray analysis. When steel wool was used as a catalyst, similarly treated turnings were placed above the bed of steel wool to supply representative catalyst samples. The catalyst was sampled after reduction, activation, and during synthesis.

Product Evaluation

Liquid product was drained periodically from the unit during steady-state periods, and samples were taken of these products for analysis. Oil samples were analyzed for bromine numbers, specific gravities, ASTM distillations, and other pertinent information. Usually the liquid was distilled into 50° C. cuts which were then analyzed by infrared spectrometry for determination of the oxygenate and olefin content. Water samples from the decanted liquid were also analyzed by mass spectrometry for their oxygenate content—alcohols, ketones, and acids.

Proportionated product gas and feed gas samples were collected in gasholders over a 24-hour period. Gas from these holders was analyzed by mass spectrometry. The carbon dioxide content of the tail gas was determined directly by hourly Orsat analysis.

Chromatographic analysis was used occasionally to determine the branched hydrocarbon content of the gaseous products.

DISCUSSION OF RESULTS

Operating Variables

The operating variables investigated in these experiments are those affecting product distribution, pressure drop through the catalyst bed, and catalyst activity. To standardize the experiments, an equal volume (0.275 cu.ft.) of catalyst was used. All catalysts had been oxidized before reduction with hydrogen. Table 1 shows a summary of experiments 7 to 17. This table lists the purpose of the experiments, type of catalyst used, induction techniques, and the important conditions of synthesis.

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TABLE 1. - Summary of experiments 7 to 17

_ 1	<u> </u>		a a					Synth		
Ex- peri- ment No.	Hain putpose	.ype ³	Catal Voids, pct.		eon- tent, pet.	Catalyst industion	Prest ^o gas space velocity vol./volhr.	fresh gas ratio,	Hot recycle: Fresh feed ratio	ratio
7		1018 steel	89.5	6,433	0.05	None. Temperature raised gradually to 305° C. in 76 hr.	600	1.5 end 1.3	60 4nd 30	2.5
8	To obtain better activity by induction technique.	1018 steel	68.5	6,990	.04	148 hr. at 270° C. at 200 S.V.H. with 1Ep:100 feed gas.	200 to 1,000	1,3	60	1.4 and 3.0
9	To decrease methane yield by increasing E ₀ 0 content of catalyst.	1018 sceel	88.5	6,990	.16	280 hr. at 270° C. at 200 S.V.H. with 1Mg:1GO feed gas.	200 10 1,000	1.3	60	2_5
10	Test activity of steel wool catalyst.	No. 6 steel wool		1,958	.16	None, because of low activity.	200	1.0 and 1.4	100	o and 1
11	Test activity of steel wool catalyst.	No. 6 steel		1,962	.12	None, because of low activity.	200 to 265	1.0 and 1.4	160 and 80	3
12	Compare use of high void turning to steel wool. Use of bauxite to up-grade products.	:1	96.0	2,469	.36	138 hr. at 275° C. at 200 S.V.H. with 1Hg:1CO feed gas.	to	1.0 and 1.3	60	2.5
13	Check four process variables: (1) Reforming gaseous products with alumins; (2) 1.4:I synthesis gas for induction; (3) Improve olefin yield using activated carbon; (4) Operate with bot recycle at 250° C		88.0			at 200 S.V.H. with 1.4Mg:1GO feed gas.	800:	1.4	40 40d 20	2.0 end 0.6
14	Induction studies and alumina reforming.	1018 STEE		7,20	T. 0	7 240 hr. at 274° C at 300 S.V.H. with IMg:ICO fee gas.	CO	1, 1 and 2		and 0.9
15	Induction studies and alumina reforming, repeat of experiment 14.	stee		6 7,20	0 .1	7 Same as Experimen	1,000	1, 1 and 2	45	2.1 and 3.5
16	Induction studies, and lover recycle ratios.	101) ste		0 7,20	.1	7 240 hr. at 270° (at 200-250 S.V.) with 1.4%:100 feed gas.		1.4 and 3	15	2.0 and 4.5
17	No induction, multiple feed.	101 ace	-			18 Noue. Temperatur raised graduall to 320° C. in 43 hr.	1,500	1.4	43 and 21	2,4

Catalyst volume equals 0.275 cu.ft. Wolume gas per volume catalyst-hour. Steel curnings except as noted.



TABLE 1. - Summary of experiments 7 to 17 (Con.)

			Sy	nthes is	(Con.)							
							el condi	rdaan		Dura-],	Ex- eri-
	Init Reactor	ial cond	HCO [· · · · · · · · · · · · · · · · · · ·	Fini cactor	es consi	IL +CO		tion,		eesc Fil
Compo	TACUTE,	• c.	conversion.	Ur age	Eumper	ature,	· c.	conversion,		hr.]	No.
In cas	Out cas	Average			in gas û	AL VER	Average	pet,	TALLO			7
300	316	305	75.3	0,9/	311	329	315	90.7	1,12	682	Activity lover than experiments with cold recycle compressor.	•
298	318	305	89 _4	1,15	321	341	329	90,1	1,15	979	Good activity; methane yield too bigh.	8
320	340	330	93,9	1,22	310	330	318	90.6	1.15	2,265	lowered mechane yield by increasing KpD content of escalyst.	9
300	303	301	c)	ტ	393	399	396	(c)	c,)	191	Unable to get good activity.	10
349	359	353	71,5	0.96	379	401	390	89_7	1.22	366	Low activity. Shut down due to earbon build-up.	11
310	330	318	87_C	1,11	-	-	-	-	-	330	Catalyst poisoned by bauxite trap operation.	12
310	330	319	85.3	1.13	311	329	318	51,1	1.85	1,145	Catalyst poisoned.	13
										- - - - - - - - -	·	
310	331	317	93.4	1.44	310	330	317	79.9	1.5	2 . 393	Caralyst poisoned.	14
310	330	318	93,6	1.29	310	330	321	91_2	1.7	3 746	ins yields higher that normal. The effect of alumina reforming was negligible.	Į
310	331	319	92.1	1.2	8 310	350	334	91.3	2.6	7 92	Unit operated satix- factorily with lower recycle ratios.	16
31:	0 330	321	88,0	1.1	300	340	317	87.5	1.1	71	Unit operated satis- factorily with multiple feed.	17

^{*}Not calculated.



As shown in table 1, steel turnings with a void volume of from 88 to 90 pct. were used in experiments 7, 8, 9, and 13 through 17. In experiments 10 and 11 steel wool with 97 pct. Tolds and in experiment 12 steel turnings with 96 pct. voids were used.

Product Distribution

Tables 7 to 12 (in the Appendix) contain the operating and yield data for the steady-state periods of experiments 7 to 17. Included in the tables are the temperature and temperature differential, pressure and pressure differential, gas conversions, analyses of the product gas, yields and distribution of products, and weight balances. The product distribution groups are C₁ plus C₂ gases, C₃ gas (propane), gasoline (propylene to 204° C₂), diesel oil (204°-316° C₂), and fuel oil and wax (>316° C₂). The oxygenated hydrocarbons and gaseous olefins are also reported.

Table 2 shows the oxygenates found in the product obtained from experiment 17. The products are typical of these experiments. Ethyl alcohol is the major component. Methanol and higher hydrocarbons are also produced. In addition to the alcohols, acetone, methyl-ethyl ketone, acetic acid, and propionic acid are found in the water phase. Esters, ketones, and higher molecular weight alcohols and acids are found in the oil phase.

Effect of Variables

The yield of oxygenates in the products from the hot gas recycle experiments is low and operating variables do not affect the yield appreciably. Usually less than 9 g./m. of $\rm H_2+CO$ converted was obtained, about the same as in the oil circulation process. These yields may be compared with that of 52 g. obtained with a nitrided catalyst which is a specific catalyst for the production of oxygenates.

The effect of variables on product distribution is shown in table 3, which is a condensation of tables 7 through 12. It lists the variables that produce appreciable changes in product distribution. These changes are also shown in graph form in figure 6.

The operating variables include temperature, the $\rm H_2$:CO ratio of the fresh gas, the fresh gas rates (hourly space velocity), and water and carbon dioxide content of the recycle gas. The effects of chloride inhibition and potassium oxide impregnation are also discussed. Pressure was held constant at 400 p.s.i.g. in these experiments. The effect of pressure on the Fischer-Tropsch synthesis has been discussed by Benson.

17Work cited in footnote 5, p. 2.



The Fischer-Tropsch Synthesis in the Oil-Circulation Process: Experiments with a Nitrided Fused-Iron Catalyst: Bureau of Mines Rept. of Investigations 5603, 1960, 32 pp.

TABLE 2. - Oxygenates and olefins found in experiment 17.

products in aqueous phase

Period	A	В	С	D	E	F	
Product water:			- ""	.			
Specific							
gravity	0.978	0.991	0.981	0.982	0.982	0.981	0.985
Acid number	17.5	14.0	6.9	8.3	11.4	13.7	22.3
Refractive	}		i				
index	1,3422	1.3412	1.3409	1.3410	1.3417	1.3420	1.3413
Product yield,		· · · · · · · · · · · · · · · · · · ·					
g./m.3 H ₂ +CO				;	l	ţ	
converted:			İ	Ì	1	1	
	114.2	124.0	129.8	121.3	122.8	123.9	122.8
C ₁ OH	0.9	0.8	0.8	1.0	0.8	0.9	0.8
C_OH	9.2	9,2	8.1	9.9	10.6	12.2	8.4
C3OH	2.3	2.9	2.6	2.9	2.8	2.6	2.1
C OH	0,1	0.3	0.3	0.4	0.6	0.4	0.4
C ₅ OH	0.3	0	0	0.3	0.3	0.2	0.1
C _s OH	0.1	0.3	0.3	0.1	0	0.1	0.1
Acetone	0.5	0.7	0.5	0.4	0.4	0.4	0,3
Methyl ethyl		i	1		1		l
ketone	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Acetic acid	1.6	1.0	0.5	0.6	0.7	0.7	1.6
Propionic						1	
acid	0.3	0.3	0.1	0.1	0	0,1	0.3
Total yield		139.6	143.1	137.1	139.1	141.6	137.0

Products in oil phase, period D (g./m. H2+CO converted)

	Product, net grams	Acid	Ester	1		Internal olefin	Branched olefin
F.D 100° C		0.09	0.10		13.28	4,24	0_87
100° - 150° C	15.2	.07	.10	.36	11.62	2.44	.44
150° - 200° C	10.2	.07	.10	.26	6.47	1.54	_35
200° - 250° C	4.6	.01	.03	.10	2.39	0.83	.15
250° - 300° C	5.0	0	.06	.13	2.22	1.11	.10
> 300° C	12.3	o	.27	.28	3,01	2.53	.65
Total	74.2	0.24	0,66	1.25	38.99	10.30	2,47



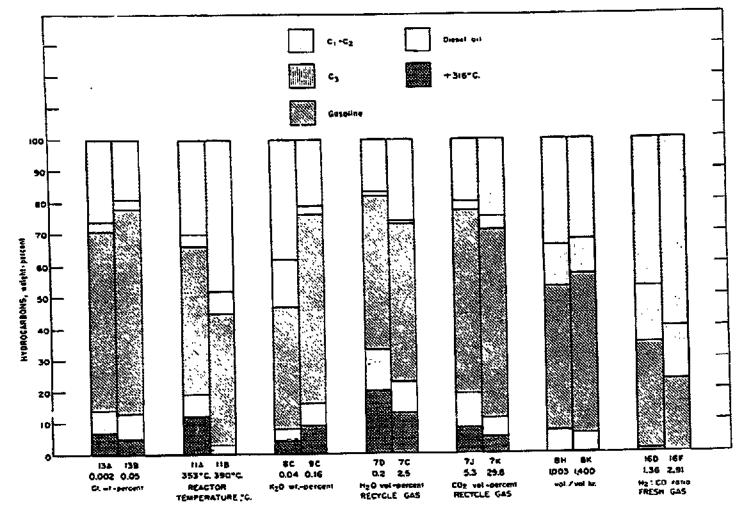


FIGURE 6. - Effect of Variables on Product Distribution.

Reactor Temperature

When the reactor temperature was raised from 353° to 390° C. in experiment 11, the yield of gaseous hydrocarbons increased and the heavier hydrocarbons decreased. As shown in table 3, the C₁ plus C₂ yield increased from 30.1 to 48.3 pct., while the gasoline fraction decreased from 46.4 to 42.1 pct. The fraction boiling over 316° C. decreased from 12.2 to 0.3 pct. Increasing the reactor temperature had little effect on the yields of oxygenates and olefins. In the oil circulation process¹⁸ more gaseous hydrocarbons and gasoline are made as the temperature is increased. However, the temperature range in the oil circulation unit was 235° to 270° C., and at these lower temperatures the yield of hydrocarbons boiling above the gasoline range is higher.

Benson, H. E., Field, J. H., Bienstock, D., and Storch, H. H., Oil Circulation Process for Fischer-Tropsch Synthesis: Ind. Eng. Chem., vol. 46, 1954, p. 2284.



٠<u>.</u>

TABLE 3. - Effect of variables on product distribution

	Reactor	15	Fresh	883	Hourly	2	Porcent	10		e it	Chlorine denosition	rton	Potassíum	Cum
	temperature	ture	를 다 6 년	<u> </u>	apace velocity		water recycle	1.n c gae	recycle Rds	t.!! c R&S	: 21	- 1	impregnation	At ion
to the transfer of the transfe	11-A 11	11-B	16-91	16-P	<u>-</u>	¥	7-0		7-1	7-X	13-A	13-B	-G	
Recycle to fresh food racto: Total	162 2,6	81 2,8	1,7	16	60	2.9	67	2.5	2,5	90	2.2	2,2	3.0	108 2,4
Average reactor temperature G.	353	390	305	313	300	329	305	330	319	319	319	\$11,	303	315
CO, in recycle gas,, pct.	4.8	5.0	5.0	2.4	10,1	10.1	4.9	6.4	5.3	29.8	5,3	1.6	9.4	r.
Water in recycle gaspct.		t	4.3	4.9	4,1	4.0	0.2	2.5	5.0	7,3	5,1	7.3	3.4	
Space velocityvol./volhr.	265	244	1,001	1,000	1,003	1,400	400	400	900	909	486	800	007	399
Fresh gas	1,41	1,23 1,02 3,58	1.36 1.26 10.0	2.91 2.61 22.4	1,29 1,16 6,51	1,30	1.28	1,31 0,97 3,21	1,29 1,09 8,04	1,29 0,73 7,68	1.40 1.13 8.31	1.46 1.73 0.88	1.28	1,33 1,18 3,87
Weight-percent of hydrocarbons: C ₁ +C ₂ C ₃ Casoline (C ₃ = - 204° C;) D[cael ofl (204°-316° C;) Fuel ofl + wax (316° C; +)	30.1 4.2 46.4 7.1	4 6 4 6 4 6 4 7 6 4 7 7	47,3 16,5 35,5 0,7	39.3 17.5 23.0 0	33.0 45.8 6.8	32,11 50,5 5,6 5,8	17.3 68.9 13.0 20.3	25.7 4.6.5 10.2 2.01	19.5 3.1 58.1 11.3 7.4	24.9 59.8 6.7	25.6 3.3.3 6.7.7 6.7	18 2,5 4,7,2 4,9	38.0 39.4 39.4 3.6	21.4 3.1 60.3 10.4 4.8
Specific yield, g./m. Ho+60 converted: Oxygenates	8.8 41.3	37.5	2,5	2,8	5.9 18.1	5.4 31.6	10,8	8,1 34,6	3.66	6.2	9.0	51.5	16.9	8.9
Potassium oxide content on catalyst	ı			•	1		•	•	+	•	ł.) 이 이	0.16
Chlorine content on catalyst		ı	1	,	,	•	,	-	-	,	80,002	30.05		•

Underlined figures indicate change in variable. Achiorine content of oxidized and impregnated turnings similar to that used in experiment 13. Ochlorine content of the discharged catalyst.



H2:CO Ratio of the Fresh Gas

An increase in the H_3 :CO ratio of the fresh gas caused a decrease in gasoline production. In experiment 16 the H_2 :CO ratio was increased from 1.36 to 2.91 and the gasoline fraction decreased from 35.5 to 23.0 pct. Simultaneously C_1 plus C_2 gases increased from 47.3 to 59.5 pct. As shown in figure 6, the product distribution shifted to the lighter hydrocarbons. The same result is also shown in table 11 in periods D and E of experiment 15 where the H_3 :CO ratio was changed from 1.41 to 2.01.

Throughput of Fresh Gas

As shown in table 3, tests 8H and 8K, an increase in the throughput of the fresh gas had very little effect on the gasoline production or the oxygenate yield, but increased the yield of gaseous olefins. An increase in the fresh-gas flow from an hourly space velocity of 1,003 to 1,400 increased the yield of C_2 - C_6 olefins from 18.1 to 31.6 g./m. of H_2 +CO converted.

Water Vapor and Carbon Dioxide Content of the Recycle Gas

An increase in the water vapor or the carbon dioxide content of the recycle gas shifted the product distribution to lighter hydrocarbons with only a slight increase in the gasoline yield. An increase in either component decreases the oxygenate yield but increases the olefin yield.

The carbon dioxide content of the total recycle stream is usually maintained at 5 pct. by scrubbing the cold recycle stream with monoethanolamine. When this scrubbing operation was suspended the carbon dioxide content of the total recycle stream increased from 5.3 to 29.8 pct. The C_2 - C_6 olefin yield increased from 39.0 to 74.4 g./m. of H_2 +CO converted. Although the water vapor content also increased 2.3 pct. at this time, it is believed that the large change in olefin content is due primarily to the carbon dioxide increase. Experiment 7 (table 3) supports this belief. Here the water vapor content of the total recycle stream changed from 0.2 to 2.5 pct. (the carbon dioxide decreased from 6.4 to 4.9 pct.); the C_2 - C_8 olefin content of the tail gas only increased from 28.5 to 34.6 g./m. of E_2 +CO converted.

Because of possible oxidation of the catalyst at this high concentration of carbon dioxide, resulting in decreased activity, it is undesirable to operate in this manner. A slight increase of the carbon dioxide content from 5 to 10 pct., shown in table 8 for periods F and G of experiment 8, increased the gaseous olefin yield by only 2 g./m. 3 of $\rm H_2+CO$ converted.

Chloride Deposition on the Catalyst

The catalyst of experiment 13 was presumed to have been exposed to hydrogen chloride that was transferred by the recycle gas from an alumina-containing trap. (The purpose of the alumina trap was to convert the terminal olefins in the recycle gas to internal olefins and to decrease the oxygenate yield. The effect of the alumina, however, was negligible.) The chlorine



content of the catalyst was 0.05 pct. after discharge. No analysis was made of the catalyst when charged to the reactor, but an unused catalyst similar to that used in experiment 13 had a chlorine content of 0.002 pct. The gasoline fraction increased from 57.7 to 66.2 pct. of the total hydrocarbon yield after the catalyst was poisoned. This was the largest percentage of gasoline in the product obtained in any of the experiments. Unfortunately, the chloride decreased the activity of the catalyst.

The presence of chloride on the catalyst increased the yield of C_3 - C_6 olefins from 41.3 to 51.5 g./m.³ and decreased the oxygenate yield from 9.0 to 2.6 g./m.³ The effects of halogen compounds on Fischer-Tropsch catalysts are described by Davis and Wilson.¹ They state that these compounds on unalkalized catalysts cause the C_2 - C_4 olefinic fraction to increase, the overall conversion to decrease, and the methane and carbon dioxide yields to decrease. These experiments corroborate their findings.

Potassium Impregnation

The addition of potassium to a catalyst increases the yield of liquid and solid hydrocarbons, and the yield of oxygenates and olefins. An increase in potassium content from 0.04 pct. in experiment 8C to 0.16 pct. in experiment 9C increased the gasoline yield from 39 to 60 pct., as shown in table 3. Figure 6 illustrates how the product distribution was shifted toward higher boiling compounds. As the percentage of C_1 plus C_2 and C_3 decrease, the yield of liquid and solid products increases. This shift is also shown in table 12 in experiment 17. When potassium hydroxide dissolved in alcohol was added to the catalyst in periods E and F, the yield of liquid and solids increased.

As the catalyst ages, the active coating on the surface of the catalyst flakes off. As a result of this loss of alkali, the yield of gaseous hydrocarbons increases with age of catalyst. This effect is illustrated in table 9, experiment 9. After 612 hours of synthesis the percentage of the product above C_3 was 75 pct.; after 1,859 hours it was 65 pct.

Table 3 also shows that when the potassium oxide content was increased from 0.04 to 0.16, the oxygenate and C_2 - C_6 olefin yield increased. The olefin yield increased from 16.9 to 44.3 g./m. of H_2 +CO converted, and the oxygenate yield from 3.3 to 8.9 g./m. of H_2 +CO. The effect of alkali on Fischer-Tropsch catalyst has been discussed by Anderson and others.

In summation, the highest yields of C_1 plus C_2 gases were obtained in experiment 11C (75.4 pct.) operating at a very high temperature of 390° C., and in experiment 16 (61.5 pct.) operating with a very high (2.94) $H_2:CO$ ratio. The highest yield of gasoline was obtained in experiment 13B (66.2 pct.) after a chloride had been deposited on the catalyst.

¹⁸Davis, H. G., and Wilson, T. P., U.S. Patent 2,717,259, Sept. 6, 1955.
²⁰Anderson, R. B., Seligman, B., Shultz, J. F., Kelly, R., Elliott, M. A., Fischer-Tropsch Synthesis--Some Important Variables of the Synthesis on Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 391-397.



Pressure Drop

The pressure drop through the catalyst bed is affected by the shape of the catalyst, the linear velocity, and the density of the gas. A comparison of steel turnings with 88 pct. voids and steel wool with 97 pct. voids shows that the pressure drop is about 50 pct. less with steel wool. However, turnings of 88 pct. voids were employed as catalyst because turnings and wool of greater void volume were less active, both on a weight and a volume basis.

As compression costs are a function of both the recycle flow and pressure drop across the bed, any reduction in either factor would be desirable. However, the flow must be sufficient to maintain stable temperature control. In experiment 16, shown in table 12, as the total recycle-to-fresh feed ratio was reduced from 44 in period C to 17 in period D, the pressure drop per foot of catalyst bed height decreased from 46 to 17 in. of water, a decrease of 63 pct. The temperature differential increased from 20° to 40° C., but there was no difficulty in maintaining control of the temperatures.

Further reduction in pressure drop may be achieved by splitting the recycle stream and proportionating the flow along the reactor length. As only part of the gas traverses the entire length of the bed, a reduction in the overall pressure drop across the bed occurs. In experiment 17 (table 12) when the gas feed was changed from single entry at the top of the reactor in period A to multiple feed (with the gas flow divided into 3 equal parts) in period B, the pressure drop decreased from 26 to 19 in. of water although the total recycle flow was constant at about 40 to 1. Continuing the multiple feed system in period C, the recycle ratio was decreased from 40 to 21 and the pressure drop decreased to 8 in. of water per foot of catalyst bed. Thus a combination of lower recycle and multiple feed slong the length of the reactor bed results in a very low pressure drop while still maintaining a high gas conversion and the same product distribution.

Another factor affecting the pressure drop is the gradual accumulation of fines during synthesis as a result of carbon deposition and the flaking of the catalyst surface. The fines collect in the lower section of the catalyst bed and cause an increased pressure drop. This factor is illustrated in figure 7.

The pressure drop increased from 16 in. of water per foot of catalyst bed at 300 hours of operation to 70 in. after 550 hours—a fourfold increase in 250 hours. The calculated pressure drop across the turnings, (neglecting the presence of fines) remained approximately the same, 12 to 15 in., during this period. This problem of pressure drop increasing with catalyst aging was present in almost all of these experiments: The pressure drop in experiment 7 increased 55 pct. in 682 hours of operation, in experiment 9, 36 pct. in 1,007 hours, and in experiment 16, 120 pct. in 416 hours. The comparisons of pressure drop are made at similar conditions of recycle and fresh feed flows.

Jimeson, R. M., and Decker, W. A., Pressure-Drop Measurements Through Beds of Granular Iron, Lathe Turnings, Steel Wool, and Parallel-Plate Assemblies: Bureau of Mines Rept. of Investigations 5541, 1959, 51 pp.
22Work cited in footnote 20.



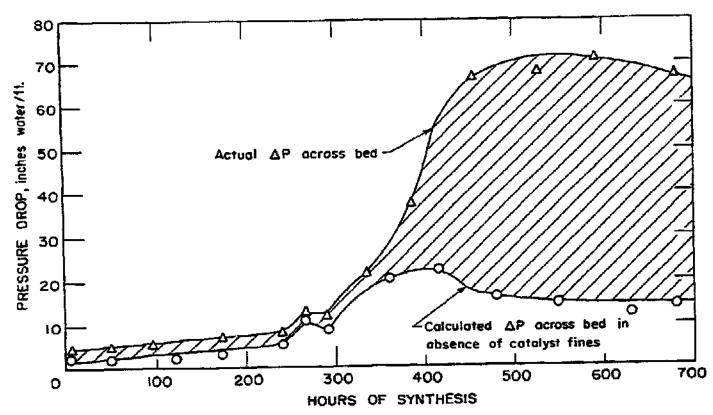


FIGURE 7. - Pressure Drop Across a Bed of Steel Lathe Turnings, Experiment 15.

Although there is sufficient evidence to indicate that the pressure drop increase is due to carbon deposition and catalyst flaking, this difficulty could not be avoided during these experiments. In later experiments, particularly experiment 21, high water vapor concentration in the recycle gas was found to prevent this condition.²³

However, with the use of turnings, recycle-to-fresh feed flows of 20 to 1 and multiple gas entry to the reactor, a pressure drop of less than 0.5 p.s.i./ft. of catalyst height has been obtained. This is sufficiently low so that it contributes a minor percentage to the cost of gasoline made by this process.

Catalyst Activity

A method of indicating catalyst activity is to calculate activity coefficients A_V in terms of volumes of feed gas (H_3+CO) converted per hour per volume of catalyst referred to a standard reference temperature. These coefficients A_V (activity per unit volume of catalyst) and A_{Fe} (activity per gram of iron) are shown in table 4. Another method of assessing activity at the

Passenstock, D., Field, J.-H., Forney, A. J., and Demski, R. J., Pilot Plant Development of the Hot-Gas-Recycle Process for the Synthesis of High-B.t.u. Gas: Bureau of Mines Rept. of Investigations 5841, 1961, 27 pp. 24Work cited in footnote 19, p. 17.



conditions used in these experiments is to consider the conversions that can be achieved when operating with maximum space velocity at the same temperature. By either of these methods the most active catalysts were those of experiments 8, 9, 15, 16, and 17. These five experiments had values of A_V greater than 140, and Ap_e values greater than 154, and had conversions of feed gas greater than 90 pct. when operating at an hourly space velocity of 1,000 at an average temperature of 319° C. or lower. The catalysts of the other experiments had A_V values less than 87, and none could be operated at an hourly space velocity of 1,000 with 90 pct. conversions.

The more active catalysts on both Ape and Av bases were those which had reactor charges of 15 and 16 lb. compared with 4 to 5 lb. used in experiments 10, 11, and 12. The catalysts used in experiments 13 and 14 exhibited low activity because of poisoning by chlorides. No reason for the low activity of the catalyst in experiment 7 is known. While sulfur poisoning was originally suspected, the possibility was discounted because the yield of C_2 - C_8 olefins was high, 29 to 50 g./m. Davis states the effect of sulfur on iron-based catalysts is to decrease formation on unsaturated gaseous hydrocarbons, so it may be concluded that in this experiment sulfur poisoning was not a factor.

The effect of alkali impregnation in the range from 0.04 to 0.36 pct. as potassium oxide upon catalyst activity is not significant in the temperature range used in these experiments. The catalyst in experiment 8 with a potassium oxide content of 0.04 pct., had as high an activity as the catalyst in experiment 9 with 0.16 pct. In experiment 17 (table 12) potassium as KOH was added to the catalyst during periods E and F. The $\rm H_2$ +CO conversion was about the same (91.9 pct. compared with 91.2 pct.) before and after this addition, but at these high conversions little increase can be expected.

In most of these experiments an induction period was used after the reduction to get the system on stream. The temperature of the reaction was raised gradually to 270° C. and maintained at that level for 10 days, then increased to the desired operating temperature. The feed gas during the induction period was usually 1H₂+1CO. In experiment 15 the feed gas used during the induction period was 1.4H₂+1CO, the gas used during the main part of the experiments. In experiment 16 the hydrogen-rich gas was again used and the temperatures were raised as fast as practical to the desired operating range. The catalysts used in these two experiments had activities (A_V) greater than 14O, indicating that the method of induction of the catalyst has little effect on its activity.

Hägg Fe₂C was the major form of iron on the surface of the catalysts shown in table 4. The difference in activity observed in these tests was not related to the carbide content of the catalyst.

²⁶Davis, H. G., and Wilson, T. P., U.S. Patent 2,717,260, Sept. 6, 1955.



TABLE 4, - Activity data for experiments 7 through 17

			•									_			ŧ
Phases, present	Hägg FeaC.	Da,	ć	• 00	•	ı	Hägg FegC, Fe, Fe3C.	Hags FeeC.	Hägg FegC, Fe,) 00		7.48 & S		ъ.	•
Are 3	66	224		157		104	102	83	92	155	9	H07	190	179	3
	8	201		141	1	72	32	78	98	145		607	171	168	59
Ha:CO ratio of fresh gas	1,3	9	7	1,35	7.7	1.6	1,4	1,40	1.84	1 40		. 	1.4	1.4	1.46
Alkali atalyst content, charge, wtpct. 1b. K.0	0.05	ò	5	•16	16	,12	.36	.13	.17	-		.17	81.	.18	£1.
Catalyst charge, lb.	14.2		4.	15,5	¢,4	4,3	5,4	15.8	15.9		۾ 	15.9	15.9	15,9	15.8
Volds, pct.	89.5		2 88	88.5	16	16	96	88	88	t	8	88	88	88	88
Opera- V	474.489	100	451-547	852-972	ı	72-96	186-258	392-464	359-393	,	396-468	712-760	423-471	663-711	528-557
0 4	\top	7.06	92.2	93,6	1	78.6	87.0	85,3	79.9	•	93.6	92.9	91.9	87.5	76.0
나는 글 등이	ture, c.	8 <u>2</u>	50	20	•	12	70	20	: 8	,	20	20	20	9	82
<u> </u>	ان	315	300	319	£	305	318	310	317		318	295	309	317	319
Space velocity, vol./	volhr.	009	1,003	1,001	(2)	306	3000	ç	193) (1	1,002	1,000	1,002	1,501	802
Bxpori-		7-L	8-1	9-X	104		12-A	;	13-A	9	15-B	16-B	17-1	11-0	13-8

Activity coefficient, activity per unit volume.

Activity coefficient, activity per gram of iron.

Obetermined by X-ray diffraction.

Steel wool catalysts; others are lathe turnings.

No data.



Chlorides reduce catalyst activity. The catalyst used in experiment 13 was poisoned during period B by chlorides present in the alumina used for treating the recycle gas stream. Table 10 shows the H₂+CO conversion decreased from 85.3 pct. before treating the recycle gas in period A to 76.0 pct. after contamination with the chloride (presumably hydrogen chloride). This poisoning effect of halides has been discussed by Davis and Wilson. 26

Gasoline Processing

A finished gasoline was prepared from period P of experiment 9 in the manner depicted in figure 8. Operating conditions for this experiment are shown

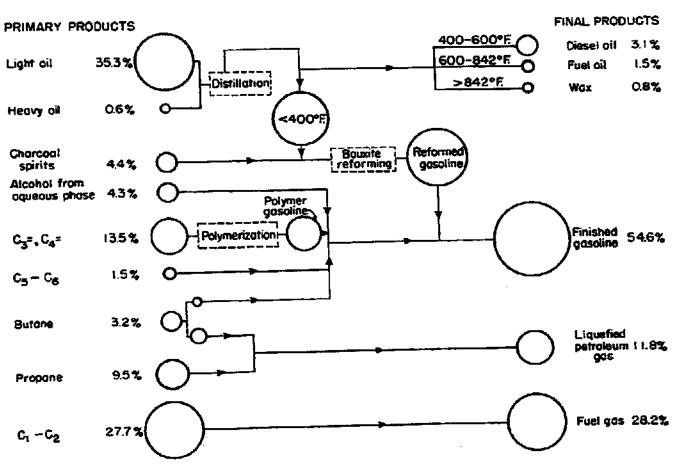


FIGURE 8. - Processing of Synthesis Products to Produce Gasoline, Experiment 9.

in table 9. The heavy and light oil streams were combined and distilled, initially at atmospheric pressure and finally at a reduced pressure of 5 mm. of mercury to prevent cracking of the heavier oil. The fraction boiling below 204° C. was combined with the charcoal spirits (a fraction collected by passing the tail gas from the reactor through activated carbon and recovering the hydrocarbons by regenerating the carbon with steam) stabilized at room temperature, and then reformed over bauxite.

²⁶Work cited in footnote 18, p. 14.



The purpose of the bauxite treatment is to upgrade the product by dehydrating the oxygenated hydrocarbons and shifting the double bond in the terminal olefins to an internal position. The conditions for bauxite treatment were as follows: A temperature of 353° C., a pressure of 25 p.s.i.g., and a liquid hourly space velocity of 1.5 vol. of liquid per volume of catalyst per hour. The catalyst used in this treatment was activated bauxite from 4- to 12-mesh. Industrially the C3 and C4 olefins would be sent to a polymerization unit for further processing. To simplify the blending procedure, a polymer gasoline, obtained commercially, was added to the reformed gasoline in an amount equivalent to that which would be obtained by polymerizing the C3 and C4 olefins. The finished gasoline contained the reformed and polymer gasoline and sufficient butane to adjust the Reid vapor pressure to about 10 p.s.i. To another gasoline sample, prepared in the same manner, the water-soluble alcohols, methyl, ethyl and n-propyl, were added in the amounts produced in the product water. The research octane number of these gasolines was determined as such, and after the addition of 1 and 3 cc. of tetraethyl lead. The results of these tests are shown in table 5.

TABLE 5. - Octane number of the finished gasoline, experiment 9

	Reid vapor		Research octan	e number
	pressure, p.s.i.	Clear	l cc. T.E.L.	3 cc. T.E.L.1
Polymer gasoline	-	95,1	–	_
Reformed + polymer + butane	9.9	77.1	85.3	90.2
Reformed + polymer + alcohol ² + butane	10.6	81.2	88.5	92.4

¹ Tetraethyl lead.

The addition of alcohol, equivalent to 8.3 pct. of the total blend raised the octane number from 77 to 81. Addition of 3 cc. of tetraethyl lead further increased th octane rating to 92. As the use of alkylate is supplanting polymer for upgrading gasoline, the gasoline from experiment 15 was blended with both alkylate and polymer gasoline. As shown in table 6, the blend containing alkylate gasoline imparted a higher octane number than the one with polymer. The alkylate gasoline with 3 cc. of tetraethyl lead had an octane number of 96.

CONCLUSIONS

The hot-gas-recycle pilot plant has been operated successfully with carbon-steel lathe turnings as catalyst. Turnings packed with 88 to 90 pct. voids were the most effective, being of high activity and low pressure drop. Turnings with higher void volumes and steel wool had lower activity.

Good temperature control was achieved operating with a recycle-to-fresh feed ratio as low as 20. At this recycle flow and with use of multiple injection of the gas into the catalyst bed a pressure drop of less than 0.5



²Alcohol, 8.3 pct. of total blend.

p.s.i./ft. of catalyst bed was obtained. The cost of recompression of the recycle gas therefore is small, amounting to a few tenths of a cent per gallon in a commercial sized reactor.

Hourly space velocities of fresh gas as high as 1,500 and conversions as high as 95 pct. were achieved. Successful pilot plant operations of 2,265 hours (over 3 months) duration were obtained. The optimum hydrocarbon production consisted of 66 pct. gasoline, 10 pct. diesel oil, 2 pct. fuel oil and wax, and the balance of 22 pct. gases. This was achieved when operating with a reactor temperature of 310°-330° C. The gasoline containing alkylate had a research octane number of 86; with addition of 3 cc. of tetraethyl lead the octane number was raised to 96.

TABLE 6. - Octane numbers of the finished gasoline, experiment 15, period D

	Reid vapor pressure,	Re	search octane	number
	p.s.i.	Clear	1 cc. T.E.L.	3 cc. T.E.L.
Polymer gasoline		96.8	-	101.1
Alkylate gasoline	-	94.2	-	103.8
Reformed + polymer + butane	8.9	84.5	91.4	94.1
Reformed + alkylate + butane		85.6	93.5	96.4

Gases containing traces of hydrogen chloride reduced the activity of catalysts; however, the product contained a greater percentage of gasoline. An alkali promoter, K_2O , on the catalyst caused a shift in the product distribution, making more gasoline and less gaseous products. The recommended quantity of K_2O to produce the maximum gasoline yield is from 0.13 to 0.18 pct.

The only operating difficulty encountered was the tendency of the catalyst to spall after prolonged synthesis. The fines produced by spalling tended to collect in the lower section of the bed together with carbon formed in the reaction. These deposits decreased the void volume and caused an increased pressure drop. After 2 to 3 months of synthesis the catalyst activity declined due to the spalling of the active layer. As a result of the loss of alkali the production of C₁ plus C₂ gases increased.

Future objectives for the pilot plant are the development of a durable catalyst that will be active for 6 months with little or no change in the product yield or the pressure drop.



APPEND IX

Tables 7 through 12 are included in the appendix.

TABLE 7. - Operating conditions and Tesuir , experiment 7

Perfect	A T	. 1	- c 7	D	2	¥	C	ii	E	J	×	1.
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vot_/volht_	100	•03	401	400	400	600	300	600	į 400	₽00	600	600
Recyclestresh gas rattor:	.1.	1		67		28	. 28	28	65	>8	60	58
Total	2.2	2.5	65 2,5	67.0	3.9	2.5	4		2.9	3.5	0	2.4
COld	3:3	2.5	2,5	2.0	<u> </u>	1 2.5		2,3	2.9	2.5	0	2.4
Water vapor in recycle gas vol. pet.	3.8	3.5	2.5	0,2	2.5	4.3			1.7	5.0	7.3	+.0
Cold recycle, pet, of total	3	4	4	100		9	1 1	•	4	4		1 -
Ha:CO retion:					١	1	1.30	1.36	1,38	1,29	1.29	1,31
Prest Kan	1.44	1.49	1.31	1.28	2.71	3.20					7.68	13.34
Recycle gas	0.97	9.9L 1.07	0.97	1.21	0.98	1,04			1	1,09	0.73	1.12
Reactor pressure	403	400	402	400	400	400	201		r –		400	14
Catalyse pressure drop in MgO/ft.	y		7	, ,	4	1 :	:	: 3	7	13	13	1 "
Catalyst temperature, * C.:						30	: 30	. Jos	305	334	314	311
Top (inics)	300	300	305 321	300	303	34					133	329
Sottem (outlet)	310 10	3le io	16	17	10	6				20		18
Differential temperature	305	305	311	305	309	31	5 31	6 31 8				315
Average	62.0	47.5	63.1	73.8	63.7	74.					1	98.5
CO conversionpcc.	95.4	*5.2	85.1	27.9	82.9							40.7
IL -CO conversion	75.3	74.8	72.0	75.6	71.9	81.	3 84.	2 89.4	77.7	` ***	""	"-"
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***************************************	1	0.7	19.3	32.0	21.8			b. e l a				
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tt tesp kageneren	- 1 4	_기 *	.9 ?	-7 #	* زه.		ا (خ	***	` '	1		
Beight-percent of hydrocarbons	ŀ	1	· ·	- {	1	1	ļ]	ļ	ĺ	. 1	
parameters:	· 1		.4 35	, 1 ,,	.3 21	ا يا	(-) :	1,3 2		- 1		·역 公
£ .£		-김 국				2.8	3	·		• • •		
	•••				9 49	ا ا ا	(°) '					3 8
Caroliar (C ₃ -204° C ₂)			8 10	.2 13	.0 1	5.# .	ሮን [(5)
Fuel vil (310°-650° C.)		7 1		· 1		<u> </u>	8	7.0				
una (450° C.)		.7	.o *	1 17		*	<u>``</u>	<u> </u>				

¹Calculated as hydrocarbons.
2Liquids not analyzed.



TABLE 5. - Operating conditions and results, experiment 8

IABLE 6. 5	A321 - 4 1	U. CV									
Period	A .	3	С	D	E	7		G	7 579-619	J 699-907	8 931-979
Hours of synthesis	52-148 200	208-256 400	280-304 ADD	316-328 801	354-39		03 3	,004	1,003	1,202	1,400
Presh gas space velocityvol./volbr. Recycla:fresh gas ratios:	200	400		971	.,		~ ·	,,,,,		-	[]
Total	100	105	105	60	60		60	60	60	60	±0 2,9
Cold	1.8	2.9	3.0	2.3	2.4		.9	1.4	2.8 1.4	2.9 1.5	1.5
CO, scrubbed	1.8	2.9	3.0	2.3	1 4.2		-2		4.4	4	4
Water vapor in recycle gas volpct. Cold recycle, pct. of total	3	3	3	1 4	2		5	ž	Š	5	5
H_:CO Tacios:	- 1	_	_	[,	-	1				
Fresh cas	1.00	0.97	1.25	1.31	1.30		.31	9.37	1.29 6.42	1.31 3.65	1.28
Recycle #85	1.11	1.32	4.33	4.51	4.80		.10 .15	1.12	1.16	1.19	1.15
Dange	0.97 400	0.93 406	405	407	41		05	409	410	414	408
Reactor pressure	-				į	1				١.,	64
catalyst	5	16	13	15	3	• 1	32	41	43	61	-
Catalyst competitute. * C.:			298	299	29		293	298	293	302	321
Top (imlet)	266 278	299 310	310	319		- 1	313	318	313	322	341
Bottom (outlet)	12	111	12	20		0	20	20	20	20	20
Niceletini combining	271	303	303	306		- 1	300	305	300	309 86.5	329 85.9
H_ conversionPCT-	57.0		87.7	82.7		- 1 "	6.3 7.8	83.6 97.7	97.5	95.3	95.6
CÖ conversion	55.8		96.4	95.0 88.0		- 1 -	2.2	89.7	91.7	89.9	90.1
He-CO conversionpcc.	57.9	91.0	1 71.3		1				1	1	1
Exit gas analysis (dry basis.	1	1		1	İ						70 7
volpct.):	46.1						1.3	43_I 4.6	38.5	37.2 10.2	
(0	42_1						5.1	1.0	0.8		
¥	0.5						5.i	9.9	10.1	1	10.4
CO	2.2			1 7			27.6	23.6	25.5		
C1	0.0		1				0.2	0,2	0.2		
	0.4		9.3			.8	8.7	7.7	1.6		
C -					- 1	.s .o	5.8	1.3 5.2	5.6		
C					*	2	1.3	1.3	1.3	1.5	
						.3	1.5	1.3	1.4		
C ₄	0.			L 0.		.3]	0.4	0.4			
				. 1		-2 [0.4	0.3 0.1			
7	, , , , , ,				- 1 -	.6	0.1	0.0			
Froduct yield, g./m. 3 Mg-CO converted:	. 0.	0 5.4	ייי ויי	٠,	٠, ٠	•-	7,7-		1		
Product yield, g./m. Mg-CO converted:	10.	9 25.	9 41.	5 42.	- 1	. ۶	39.2	70.0			
Garante Areas Same agent		- 1	7 0.			.6	0.5	0.1 26.5			
	.					.0	4.9	6.3			- 1
***	_				[ï	24.1	25.5	1 -		
	- 1					1	6.9	8.2			
# · · · · · · · · · · · · · · · · · · ·	- 1	,-,	- 1	3 9	.2	1.6	8.8	8.5			
C_ =	- 1	4 1.	3 2.			2.3	2.8 2.6	3.0 2.4			
A	- -	8 0.			- - 1	L.2 D.0	1.4	. 6.3		5 0.	4 0.0
A	_	.0 0.	0 0			5.6	0.7	0.0	0.		- 0
A	- I			0 49	_6 5:	2,3	57.4	49.0			
Aqueous phase	93	** I	5 98	8 98			102.6	93.	. 1 –		5 4.3
Addedre busher	. 3	.3 4	- 1	· .	- 1	4.8	5.3 0.7	6.		- 1	0.9
Order oxizeners		.8 0				6.3	96.6	88.	9 104.	9 107	5 110.1
		.2 77 6 414		TT 1	T:	2.4	338.4	359.			
COTotal hydrocarbon recovery	193	T:		.1 179	.7 17	6.1	180.2	175.	-		
Whater and and TAPAMETY	_~~	.4 201	4 197		* . I	7-2	198.6	197.			- 1
a	e. 92	.4 98	.7 99	.Z 91	1.9 9	8.5	98.7	} ,,,,	·-	_	·
madenerhous recovered, 15./1,000 ft.	- 1		.1 10	.3	9.9	9.8	10,4	9.	8 10	.2 10	_4 10.6
	•••	.0 10	**	•-	-	į	-	1			1
Weight-percent of hydrocarbons	- 1			1	1	!		ļ			o 32.
recovered: G-G	1.1			1		8.7	35.8		". l		4 11.
G-G	:	2.0 6				13.7	13.4 43.4		· · · · · · · · · · · · · · · · · · ·		0 50.
Gasolina (C ₃ = 204° C ₄)	4				5.3	5.0	6.2		.0 6	.8	1.1 5.
#	-				0.2	0.2	0,2	9		7. 1 .	0.1
Fuel oll (316°-450° C.)	2				1.1 <u> </u>	0.8	1.0	0	.3 9	-4	0.4 0.
Wax (> 450° C.)							<u> "</u>				

^{&#}x27;Calculated as hydrocarbons.



TABLE 9. - Operating conditions and results, experiment 9

						- 1		(E)Ons			1	. 1		 T		0	P		T	Ř
Period	A	3	<u>c</u>		뭐	540-	F 588-	C	H 660-	756			72-		N 092-	1,188-	1,260		8- 1,	667-
	180- 252	324 348		- :	20- 63	504	612	660	732	828				,068 1,	188	1.260	1,368			859
Fresh gas space	1		_				801	801	801	۱	ر ایس	001 3	002	,002 1,	.001	1,001	1,001	1,00	1 1,	001
velocityvol./volhr. Recycle:frosh gas ratios:	202	31	2 3	99	207	#90	801	901	ou t	1	l l	٠, ا	٠,٣٠١			-	ľ		i	
Total	114	11	4 1	108	60	60	60	60	60		60	60	60	60	2.2	60 2.2	60 2,1		9	5.2 5.5
Cold	0.8	2.		2-4	2.5	2,4	2.5	2.5	2.1			2.3 2.3	2.3	2.3	1.1	î.i	1.1			1.2
CO ₂ scrubbed	0.8	2.	'1 '		2-3		2.3			1			- 1		- 1	_		١.		
gravolpct.	3.6	- .	.3 4	6	4.4	0.5	5_7	-	6.:	1 6	ا (9	6.1	6.1	5.9	6.8	6.5	6.4	5.	٠٠	4.5
Cold recycle, pet. of	_		_	اء		4	4	4	1 .		4	4	4	4	4	4	4	, j	4	4
Cotal	1		긕	겍	ㅓ	- "	-	-	·	- [7	1	- 1		1		1			
Fresh gas	0_99	1:	1 1	.33	1.33	1.31	1.30	1,31	1.3	1.	35 1	38		1.37		9.07	9.76			1.30 6.23
Recycle gas	1.36	ļ 2.9	94 3			18.64	6.79		12.8	2) 13: 2) 11:	53 18	.57 2 .24	1,22	1.23	1.25	1.21	1,2	i i		1.15
Usage	0,88	1	ᅃ	.18	1.15	1.21	1.17	1,15		<u> </u>	· *				1	_	1	1		407
Reactor pressure	402	4	DI .	402	400	-01	603	403	40	3 4	03	405	406	407	408	409	404	' "	D6	407
Pressure differential		Ì	-	- 1	Ì				1		- 1	- 1	1	ļ	- 1		l	ì		
across catalyse	4	ļ.	7	8	7	8	14	16		7	27	28	31	31	37	39	4:	3	42	36
Catalyst temperature,	-	1	1	٦	- [_	-	, "		1		j	- 1	ļ	i	i				
* C.:						***	1	315	32	ب ای	320	310	310	310	310	209	330	o 3	10	310
Top (inlet)	270 281		20	310	303 323	310 330					340	330	330	330	330	330	33	0 ∤ 3	30	330
Bottom (Dullet) Differential	- E-	1 -								ı			ا۔۔	المم		21	1 2	١	20	20
Democratorer	1.		11	12	20	20				10	300 30	20 319	20 319	20 319	20 319	319	, –		18	318
Average	27:		14	317	311 80.9	320 92.2						37.6	88.2	88.4	89.8	89.0	89.	5 89	0.	85.9
He conversionpcs.	76.4			0.CE	93.3							98.9	99.2	98.8	98.6	98,4		- 1 - :	3.2	96.9 90_6
CO conversionpct.	72	-, -		87.7	86.3				6 9Z.	.5 9:	3.9	93.6	92.8	92.8	93.5	93.1	93.	٠, اد	2.9	70,a
Exit gas analysis (dry	}	1	-	- }			Ì	1	1		- 1	- 1		- 1		1	1	- 1	. 1	
basis, volper.:	48.	٠,	1.5	51.1	51.1	41.0	47.5	53.	5 46	4 او.	0.2	60.7	46.1	43.7	39.2	39.8			3.3	46.6 7.7
Hg	1			13.5	13.7	2.3	7.0	12.	9 3		3.1	2.0	2.3	3.3	4.L	1.4			1.1	1.0
N	0.	2	1.1	1.9	1.8						0.B	1.6	0.0 5.3	0.6 5.5	10.2			2 1	0.3	9_9
CO	10.		5.7	5.3	5.0							25.4	25.4		22.2	22.4	24.	5 2	0.7	16.5
G	3		1.8	13.3	14.7	4		-,			0.9	0.9	0.6	0.6	0.7			•••	7.5	0.5 6.D
C ₂	e.		3.6	3.6	3.1	7.	1 5.	9] 4.		-1		9.5	9.7	9.3	9.0 4.2		- 1		3.2	3.0
E. 3	,	3	4.2	4.6	÷.,			8 3.		-6	5.3	4.5	3.8 2.9		4.3			.1	3,7	3.1
C	.) ប.		1.0	1.2	1.					.3	2.7	2.4	2,1	2.0	2,3			!	2.2	1.9 1.0
C	0.		2.2	0.4				7 0.	3		1.0	1.2	1-1	1.1	1.0 0.7				1.1	9.5
G	Ŏ		0.9	0.8	0.1	s 1.	5 0.	* 1		!-?	0.8	0.7	0.3		0.7	1	- 1 -	.3	0.3	0.2
C	-1 '		0.2	0.1						2.2	0.1	0.2			0.1	0.	2 0	-2	0.2	0.1
G, -,	-		0.5	0.2	0.					0.0	0.0	0.1		0.1	9.0) o.	0 0	-1	0.0	0_0
Product yield, p./a.	٠ ٢	•	٧.٠١	•,•	٠.	` `	`\		Ī .	- 1	- 1					l	1	- 1	- 1	
No CO converted:				'			9 20.	.8 23	6 2	2.5	26.2	27.1	28.6	28.5	25.1		-		:=.5	23.6
Ć		-5	9.0	17.7 5.7	## - F				.=	2.4	1.7	1,8	1.2					.0	1.3 j	1.3 15.6
G		اد:	6.2	11,3	12.	aļ 12.	1 13				19.8	20.9			20.0	-			10.1	10.7
£3	. 8	.6	(و. پند	19.9							15.0				14.0	0 14	5 15		11.6	11,4
C	-1 9	-2	3.7	5.0 11.7			7 10		1.6	8.8	10.3	9.7	8.	8.6	9.5		1		8.8	8.9 5.4
C_F	<u> </u>	.0	4.2		۵.	3 7	3 4	_3 4		5.3	5.0	3.7	6.1		3.				5.5	
G _F	. 1	.7	4.5	5_4	4.	.8 5	·ᅴ ţ			3.4	3.7 1.5					1 1	.5	LL	1.9	1.4
C,		-0		1.0			·9 1			0.9	0.8	1.3	3 O.	6 0.7	0.1			0.6	0.1	1.2
Ç. •	·· }	.2	1.0	0,0	0.	,ol 0	.o a	.0 (- Al	n 71	0.0	0.3	5	0 20.1	78		1 -	0.6	65.2	
G		ا ء	a</td <td>70.1</td> <td>78.</td> <td>.9 77</td> <td>-9 87</td> <td>.9</td> <td>1.3</td> <td>8.3</td> <td>72.4 134 ?</td> <td>13.1</td> <td>51. 6 128</td> <td>2 72.1 9 126.</td> <td>134</td> <td>5 128</td> <td>- 1</td> <td></td> <td>13.4</td> <td>97.1</td>	70.1	78.	.9 77	-9 87	.9	1.3	8.3	72.4 134 ?	13.1	51. 6 128	2 72.1 9 126.	134	5 128	- 1		13.4	97.1
Agueous Share		7.7	07.7	107.3	111	2 134	.8 131 0	.9		7_1	6.0	5.1	8 6.	2 5.7	7 > -	و او	.7	4.8	5.7	5.1 0.9
CC-OH	•	· al	7.3	2.5	2 2	5 2	.5 2	4	- 1	2 2	4 7	1 1	1 II.	1	1	2 120		0.9	1.2 5.601	91.1
Other oxygenates						1			ַ בַּבְ	27.7	127.0	123.	7] 121. 3] 302	6 119.	288	.5 120 .5 297			303.5	301.8
CG	1	. 9	294_8	315.4	326	.4 294	ינונן פי.	.0 32	• 7	""-"	730	,,,,,,	7 302.	305_0		-		- 1		
Laul dag selata		, إي	26 L	201	8 177	.6 173	6 18	2.5	ູ່ນ	58.9	177.4	183.	1 179.	8 178.	178.	.6 177 7 201			155.Z 201.7	
Theoretical recovery	1 20		.06.0	203.	7 202	.9 20	.6 20	3.2 20	3.6	02.4	201,3	J 200.	7 200.	.9 200,	. 201	., 50,	` *`]
Overall weight balance	1								1	أو رو	97.5	100.	3 49	.0 99.	3 98	,2 9:	7.8	7.9	92.5	97.3
	E. 7	9.0	86.3	93.	5 97	·0 4	7.5 10					1			1	1		ا ۾ ۾		8.3
Hydrocarbon freevery.	ı	5.3	7.1	8.	ء او	.5 1	3.3 1	0.4	ļ	9.7	10.3	3 10.	.6 10	.3 10.	10	·* 10	9,1	10.0	8.9	` ~
<pre>ib./1.000 St. fresh p Usight-percent of</pre>				Ţ	1 '	~ ~		ļ	Ì	l		1	1	1	1	1	1	- 1		
hydrocarbons:	1	J			ار	. إر	/_a 2	اوره		22.6	26.4	27	.2 29	.0 28.	8 26			28.9	26.3	
CC	- 1		15.8 2.9					4.1	Ĭ	5.9	7.	5 8 .	. 31 5	_21 9.	.6 7	.8	4.7	8.7	7.5 \$8.1	
Casoline (Car-204 (0.8 4.9						9.3		59.7	56.	1 54	.0 55	.2 52	.B SS	·-· '	~•' <u> </u>			
Diesel źwel		- 1		1	J	, ,	9_8 3	2.0	j	9.9	8.	a] 9		.6 7		-	8.0	7.0	7.	
(205*-316* C.)	::(:	2.6	11.	10.	[o] `	1.2	اء. ه	0.9]	0.4	١ ٥.	1 0	_2 0	2 0			0.1	0.1	0.3	
Fuel oil (316*-450* (i6.i	4.		ě		2:0	2.8		1.5	<u> </u>	- 0			• • •					<u> </u>
droca				•																

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TABLE 10. - Operating conditions and results, experiments 11, 12, and 13

				Experi-	Experipent 13										
j -		Experiment II		ment 12		B)	C	G	Ha						
Hours of synthesis	68-21a	236-28-	318-366	186-258	392-464	528-557	£19-6	91 747	-819 8	73-945	969-1,017	1,641-1,089	1,113-1,145		
Tresh gas apace			1	1 !			ı			600	601	601	600		
velocity vol./volhr.	265	244	241	300	799	802	80	" [601	800	967	1			
Recycle: fresh gas Tazina:	262	81	82	54	46	37	4	3 I	36	35	31	31	17		
Cold	2.6	2.8	2.8	2.5	2,2	2.2] 2.		1.5	1.0	0.7	0.6	0.6		
CO_ scrubbed	2.6	2,8	2.8	2.5	2.2	2,2	2-	1	1.5	1,0	0_7	0,0	V."		
Cold recycle, pct. of	2	۱ ،	3	4	5	ه]	5	4	3	2	2	4		
Local	<u> </u>	1 ,	1 1	· •	•	· -	1	- I	- 1	_		l			
Fresh gas	1.4L	1,23	1.32	1.33	1.40	1.46	1.3		1.40	1.47	1,35	1.33	1,53 1,26		
Recycle gas	4,32		2.65	6,22	8.31	0.88	1.4		1.65	1.43	1.74	1.31	1.85		
Usage	0.96 400	1_02	1,22	400	399	401	40		400	401	401	402	402		
Reactor pressure	*****		1	1	1]	.		1			43	39		
im, M_O/ft, catalyst	8	2	9	1	111	16	1 :	28	25	49	36	***	"		
Catalyst temperature, C.:			379	310	310	310	30	10	310	310	311	311	311		
Top (inlet)	349 359				330	330		30	330	330	330	330	329		
Bottom (outlet) Differential temperature				20	20	20		20	20	20	19 318	19	18 318		
Average	353				319	319		19	319 81.7	318 70.9	63.7	57.4	34.9		
H, conversionpet.	60.3				77_6 96_2	81.2 68.6			84.4	70,1	60.3	58,3	45,4		
CO conversionpcc.	87.J				85.3	76.0			82.5	70.6	62.3	57.8	57.1		
Majer vapor in recycle	/		1		1	!		_ l	ا ، .	9.2	9.5	9.0	10.0		
gasvolpct.	3.2	: 2.5	2.4	4.8	5.1	7.3	•	-3	7_6	7,2	J 3.3	,			
frit gas analysis (dry	1	1	1	1	1	i	1	١,			1		1		
basis, vol.~pct.):	63.3	49.7	,] 32.4	57.2				.>	43.1	46.8	46.2 37.4	48.9 35.9	50.1 39.7		
Ç0		13.9	1 12.4						26.2 0.1	32_7 0.9		0.5	0.6		
N	1 0-:							7	5.0	4.8		4_9	2.3		
CO	10.							.8	ואנט	7.3	5_6	4.7	3.1		
G	1.				2.2			0.9 0.8		0.9			0.9		
£	2.	5 5.	1 4.			3.6 2.0		4.7		2.0 2.2			1.3		
C-+	. 1					3.8 3.2 1.1 0.6		3.5 3.0 2.1 1.8		0.7		0.5	0.3		
<u>C.</u>	. 📭					1.5 1.4		1.7 1.6		1,1	. 0.8		0.6		
C	0.					0.	2 1	0.5	0.4	0.2			0.1		
G			-, -	0 0.3	3 0.4			0.5 0.		0.7			0.0		
C	., 0.							0.0	0.0	0,0	0.0	0.1	0.0		
C. +	. 0.							0.0	0.0	0.0	0.0	9.0	0.0		
Ga	• 0-	· ·	٠, ٠.	·*				ł	1	1	1	l	Į		
Product yield, 5./0.	1	1			_	.		7.2	28,3	25.0	5 27.0	25.7	22.3		
Ē	. 36.			.1 20.				3.1	3,1	6.		7.8	17.4		
C	_ I B.				- 1		7 2	7.1	17.1	14			11.0 27.6		
G	18. 18.			<u>ت</u> ا اڌ	3 19.	9 24		8.3	18.5	23.			6.5		
	_ [B	9 10.	6 9.	.6 5.				1.1	11.1	15.			17.5		
) I.D.			.s ?. 2 5.			:i '	4.5	3.8	3.	3 2.	6 5.3	3.2		
C	• I • •		.4 3 .6 0	.2 5. 6 3.		4 3	.5	4.7	4.6) <u>6</u> .			0.0		
Cg				0 2.	4 3.		-4	1.1	1.0	2.		T . T.	0.0		
Catanatanananan	ō	_0 0		.0 0.			:6	0.0	0.0			0 0.0			
C	0			3 83			اة:	75_8	71.2	74.					
<u> </u>	25 109			7 121		4 206	.2 L	57_0	148,7		- 1				
Aqueous phase			_2 1	_0 7.	.3 7.		-3	3.5	1.E 0.4				2.1		
Cr-CaOH2	2				.4 1. 6 119		6 1	0.3 53.2	145.2		4 164.	.0 264.5			
н.о	100			3 308			-: -	15.8	225.9	194					
CO ₂	376 209			4 179				79.2	175.2	102	.1 178.	.3 189.9	, , , , , , ,		
Total hydrocarbon recove Theoretical hydrocarbon	اد:		1	- I	1	. /		01.4	201,5	202	.1 202.	2 202,0	202.9		
TOCOVETY	199	-9 198	1.3 194	2 202	.8 202	.1 204	``` `	~~		1	ĺ		.		
Duerall weight balance	- 1		ہما ہ	عو ا د.د	.5 98	.9 97	7.2	94.9	94.9	98	. 9 96	.3 95.4	99.6		
	:- ²⁰⁾	1.2 97	2-1 91			·	- I	اہہا	٠ ـ ا	,	.0 6	6.6	8 6.1		
Bydracarbon recovered, 1b./1,000 fr. fresh ga	و ا۔و	9.3 1	1.3	9.9	.8 10	.0 0	8.9	9.5	9.0	'l "	·" °	-	-		
Weight-percent of bydro-	- I	-	1		i	ł	- [ĺ	1	- 1		_		
cathons recovered:	- 1		۔ ای	5.4 22	9 25	.6 2	8_8	26.4	27.1			.2 25-			
Ca eligana e e e e e e e e e e e e e e e e e e						.3 j	Z_5	6.7	6.4		• •	8 61.			
Casaline (C ₃ = - 204° (3 4		2.1 2	2.0 54	. 9 57	7 6	6.2	59.3 4.8	58.	- 1 .		5.3 5.	9 6.9		
m(see 1 all (204°+316°)	:_}i	7.1					7.7 3.5	2,1	1.4	4 3	2.8	2,1 1.			
Fuel atl (316°-150° C.	.)- '						1.3	1.2	0.	3		0.	<u> </u>		
C. A SOT (C.)	1			arbon tr				Calculated as hydrocarbons.							



TABLE 11. - Operating conditions and results, experiments 14 and 15

	Experim	ent 14		Ex	periment	15	
	A L	B B	Α.	B 1	c ¹	D	E
Period.	153-225	369-393	108-180	396~468	492-564	572-644	668-74D
Fresh gas space velocityvol./volhr.	268	1,000	250	1,002	1,002	998	1,000
Reevele:fresh cas fatios:		-•					
Total	96	43	77	46	45	43	42
Cold	1.9	0.9	2.1	2.7	2.6	2.7 2.7	3.5 1.3
CQ. scrubbed.	1.9	0.9	2.1	2.7	2.6	2-6	8
Cold recycle, pct, of total	2	2	, ,		•	, ,	•
Ha:CO ratios:	0.00	1.84	0_99	1,40	1.39	1.41	2,01
Fresi gas	0.98 0.84	4.88	1.02	9.82	6.88	12.23	18.32
Recycle gas	1.03	1.52	0.98	1.29	1.29	1.29	1.78
Usaga	400	401	400	399	400	400	399
Reactor pressure	6	47	7	62	66+	66+	66+
Catalyst temperature, * C.:	1		1]			
Top (iclet)	270	310	265	310	310	310	310
Borrom (outlet)	280	330	275	330	329	330	330
Differential temperature	10	20	[10	20	19	20	20
Average	274	317	270	318	519	321	321
He conversionpct.	79.7	74.3	73.9	90.3	92.1	90_4	87.6
CO conversion	76.2	90.1	74.5	98.2	98.9	98.5	98.4
H.=CO conversion	77.9	79.9	74.0	93.6	94.9	93.8	91.2
Warer vanor in recycle cas	4.2	14.6	1 3.5	3.9	3.0	4.0	4.6
End and applicate (dwg hasis, Vol.+DCE_):	1 .	1	1	1	ر مو آ	26.9	34.8
givering for a resident for a reside	35.7	58.6	42.3	28.5	24,1	2.2	1.9
CO	42.5	12.0	41.3	2.9	1.4	2.2	2.1
*	0.6	1.2	0.7	4.9	4.7	4.8	4.8
CA.	5,2	4-1	5.1	40.6	42.6	41.3	38.3
	8.1	11.3	0.4	0.3	0.4	0.2	0.4
C32	0.2	3.8	1.7	9.6	10.4	10.0	8.1
		3.5	1.0	1.1	1.4	1.3	0.7
C32		1.4	0.6	6.1	6.2	6.8	5.5
Cz	0.9	1.8	0.6	1.2	1.4	1.2	0.7
P _	1 0.7	0.5	0.3	2.1	2.5	2,1	1.7
G	0.3	0_6	0.3	0.4	0.6	0_4	0.4
Ca*	0.1	0.1		0.5	0.5	0.5	0.5
Cg ,	0.1	0.1	1	0,1	0.2	0.1	0.1
	0.0	0.0		0.0	0.1	Į 0.0	0.0
Cg	'	1	1	i	i .	i	i
Consequence of the contract of	21.5	28,2	14.5	59.6	60.3	65.2	71.4
G_=		4.7	2.5		1.0		1.3
63 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	14.3	18.6			28.7	31.1	29.2
		24.9			5.6 25.3		29.2
PT		10.1					4_8
a	~~~~	17.1				1	12.0
A	- 1		'	T			3.4
A ^T	+ I	· · · · · ·		'		1	4.3
	*	-		l			1.4
A ⁻		1				0_0	0.0
A	-					. 23.9	18.
A21	*			92.5	102.5	98.1	151.5
Ydreone byggs.					1.8		
Ca-CaOHa				7 0.7			
Other oxygenates	84.5	. 1		89.7			
EgO	305.0		2 337.1				I
COTotal hydrocarbon recovery	154					1	I
Total hydrocarbon recovery	202		1 204.				·
Theoretical mydrocarpon according to the control of	87.			_	- 1	_ 1	
Overall weight balancepct Hydrocarbons recovered, 1b./1,000 ft. fresh gas	7.		6 7.	9 9.5	9 10.	7 10.9	10.
Weight percent of hydrocarbons recovered:	- i	}	_	_	_		. ==
	23.						
				'- I - -			. 1
						- 1 - 4	
			- 1		_	- 1	
- 4 /9769_1507 C }	!				1 .	- t .	_
Wax (> 450° C.)	0.	3 0.	9 6.	, u <u>. u</u> .	<u>~ </u>	<u>- 1</u>	

Alumina reformer in service. Calculated as hydrocarbons.



TABLE 12. - Operation conditions and results, experiments 16 and 17

			Free	FT 1941	nt 16						E	spect.	nt nt	17			
	. 1	3 T	<u> </u>	B	T E	Ti	7	G		15.0	C	•		E ₂	7	G	
Per 10d	156-	344-	464-	632	71.2	- BX		872-	219-	Z71			23-	507-	591-	663- 711	
Rouge of synthesis	228	416	536	704				920	267	339			<u>".</u>	579 [1,002	639 1,002		
Presh gas space velocityvol./velhx.	250	1,001	1,000	1,00	1 1,00	20 1,1	001 <u>]</u> 1	,000	1,002	99	/ +,•	" "	~~	ا تست		-,	
Parada da da Parida -	931	44	24	lı	, i		16	16	43			21	41	45	46	21	
Total	2,0	2.6	2.6		6 2	.6	4.5	4.4	2.4				2.5	2-5	2.5 2.5	2,5	
CO generalized	2.0	2,6	2.6			.6	0.0	0.0				ú	2.5	2.5	2.5	12	
Cold recycle, pet. of sotal	2	6	6	1	5	6	28	28	6	1	6	**	۳	٦	_		
N YOU TELIOR:	امد			j.,	ر ای	35 2	.91	2.94	1.3	1.3	a 1.	42 2	.40	1,37	1.40		
Threat are	1.40	1.42	1,40 8,24				35	16.64		8.7	8 10.	93 11	.82		11.67	9.36	
Recycle gas	2.55 1.18	1,28	1.31				61	2.67		7 1.2			-24	1.20	1.23		
Usage	401	403	400				401	400			1	00	4였	400 34	400 39		
Reactor pressure	7	27	-	6))	17	59]	12	14	24	`	^{[9}]	•	33	J-4	-	1	
Complete franchistature, T.C.:						285	290	310	310	3	ւսև շ	195	300	300	300		
M-11	265	310 331	310 330			105	330	350				130	320	320	220		
## (## (## (## (## (## (## (## (## (##	275 10	1	20			20	40	40	2		20	35	20	20	20		
Differential temperature	270		31		05 2	75	313	334				16	309 57.5	309 86.6			
Aueragepcc.	70.1	88.1	52.				98.0	89.4					98.1	98.7			J
	83,4		98.				98.4	98.		-,	1 -		91.9	92.7		87.5	
	75.6		94. 3.			<u>- 2</u> :	او.ه	5.0				5.1	5.7	\$.7		7 5.3	,
Tite and the second of the sec	4.0	4.0	i "	ገ ፣	- 1	1	1		\ _		1	ا _ ا		,	ر مر ا	ol sa.o	
Pure des analysis (dry bests, volPet./-	56_9	36.0	26,	5 29	.1 3		38.0	36.					44.9 3.8	48.0			
EQ.	22,3		3,	,2 2	-9]	3.5	3-7	3.		,-		4.0 0.0	0.0				
	0.0			-		9.0	0.0	0.				4.8	4.8				,
	4.5					5_0 7.4	2.4 39.6		- 1 -	·		8.4	26.8	25.0	· 23.		
	,			•-1		0.0	0.0			5 (7.7	0.4	0.3				
						9.2	9.1					7.5	7.6				
	, -,				0.7	0.7	0.5				3.7	3.4	2.9 4.6		- 2		
Call	1.		4 7			7-민	5.9				2.0	2.0	1.5			1 1.7	7
						0.8	0.5 1.7				1.0	1.0	1,3	1 1.	0 1.	0.0	
~~	,				2.1 0.4	0.3	0.2			5	0.5	0_5	0.6				
					ŏ.4	0.3	0.4	. 0.	3 0		0, Z	0.2	0.3				
					0.0	0.0	0.0				0.2	0.2	0.0	-: -		0.0	
					0.0	ᅃᄱ	٥,0	가 오 .	.기 이	-0	0-0	٧٠٠١	U_1	٦,	~ } ~		
Cg 2200ct yield, g_/m, Hg-GD convexted:	1	1	1		. ا. ـ	ا۔ ۔۔	72_1	73	2 20	. 1 3	3.2	34.3	32.	s 31.			
					6.6	51.7	0.0	-1			1.6	1.0	0.4			-9 -4-	
			'TI _:			25.2	32.0	T	0 11	3.2	.6.3	7.4	18.				
					2.6	2.9	7.	s 3			2.4	12.7	10, 16,			*	
						26.5	30	-1			8.7	أدوا	9.			9 9.	
C3	6		.5] (6.5	4.5	4.5	3.			7.2	5.6	5.6	5.	-		.9 4.	
		.리 끄			12.2	9.9 1.8	11.			3.8	2.7	2.7	3.		- , -	.6 3.	.7 .8
				3.0 2.5	3.2	2.0		· .	4.4	1.5	1.1	1.1	1.				.9
				0.8	0.6	0.0	0,			2.0	0.6	1.3	1.				Ö
G	''l â		اه.	0.0	0.6	0.0				8.8	0.0	70.9				9 96	.3
G	62	.0 38	.7 3	3.5	35.3	36.4	13. 209	_		9 6 1	39.6	143.1	137	.1 139			•
Aqueous phase	102		-2 20	1.3	2.1] T 3.			7.6		7_2					0.0
Other exhibitions of the control of			~ al	n al	റ ചി	0_2	i o	3	ا کہ ہ	1.7	1.9	1.2			. al	4 170	Ď.
Orber exygenates	·	3 99	22 اوّ ا	×.3 1	03.3	101.1	206	.이 20	6.7 12	ון כים	78.7	134./ 186 A	1256	3 28	6 28	0.6 128 6.8 304 2.1 189 0.8 202	2
No																	
Total hydrocarbon recovery	15	2,0 17	3.2 1	73.5 2	37.0	165.3		-31 18	1 4 1	ادو	00.2	199.8	199	_9 ZDI	0.5 20	0.8 202 9.5 99	1.0
	20:	L8 15	.9 1	36.6 1	97.0	22.0	95	3 9	3.6	8.6	96.4	98.2	98	1.6 9	7.4] 9	9.5 99	٠,٠
Overall weight belance	t. 9:	1-5 커	•••∣ :	3	****					1	[]		.[، اء،	0.7 2	عد أو و	0,3
Sydrocarbons recovered, 15./1,000 fc.	- 1 -	7.2 1	: ا ₁₋ ہ	10.2	10.4		5 20] -	
		· • • • • • • • • • • • • • • • • • • •					_	. این		28.8	29 1	30.4	2	3.al 2	6.7		2.0
Weight percent of hydrocarooms recovered.) 2	ء _ا م	4.7	46.7	47.3	45.	김 39	'-김 (16.2	7:3	7.7	7.	2 3	0.0	7.0		3.6
C3 - C4		7 W 1	J_81	10-21	74.0-		6 25		22.3	52.6	53.6	55.	31 34	4.2 3		56.1 5	
		5.6 3	7-학	34. 김	35.5 0.7	ו מו	oł C	o_ol	0.0	7.0	4.5	5.	7 1	5.Q	5.0	7.9	5.4
		8.9 0.0	1.7 0.2	1.6	0.0	0.7	ol c	-0	0.0	3.1	1.5				3.3		5.2
			6.6	ŏ.ō	0.0		0 0	0.0	0.0	1.5	3.3	<u> </u>	2		2,01		
Wex (> 450° C.)																	



Alemina reformer in service.

Split recycle stress.

Added 6 g. of potassium.

*Colculated as hydrocarbons.

GLOSSARY OF TERMS

Fresh gas	Synthesis gas composed essentially of hydrogen and carbon monoxide.
Fresh gas ratio	Volumetric ratio of hydrogen-to-carbon monoxide, dimensionless.
Usage ratio	Volumetric ratio of hydrogen consumed-to- carbon monoxide consumed during synthe- sis, dimensionless.
Hourly space velocity of gas, S.V.H. (in tables)	Volumes (S.T.P.) of gas per hour per volume of catalyst. Cubic feet per hour per cubic foot of catalyst. (S.T.P.) refers to 0° C. and 760 mm. Hg pressure.
Conversion, percent	Extent of conversion of raw materials such as B ₂ +CO:
	N Aut v 100.
$(\mathbf{H}_{3}+\mathbf{CO}) \text{in - } (\mathbf{H}_{2}+\mathbf{CO})$	dimensionless.
(H ₂ +CO)	o) out x 100, dimensionless.
	Weight of any component or components per unit volume of feed or converted gas, pound component per cubic foot of gas or gram component per cubic meter of gas.
Specific yield	Yield of given product per cubic meter of converted synthesis gas, gram per cubic meter converted (H2+CO).
Space-weight yield	Volume of gas converted per hour per weight of catalyst, cubic foot (\$.T.P.) per hour per pound of catalyst.
Catalyst activity	Quantitative relationship between extent of conversion and operating temperature at any time during synthesis, usually judged by temperature required for a certain conversion at a given space velocity.
Activity coefficient	. Indication of catalyst activity the larger the coefficient, the more active the catalyst.



 $A_v = 1.241 \times 10^{-8} \times S \times 10^{4130/T} \times \log_{10} (1/1-c) \text{ where}^{27}$

s = hourly space velocity

T = absolute temperature, * K.

C = conversion

AFe = Av divided by catalyst density (gram per cubic centimeter)

Massive iron catalysts............... Catalysts made from steel in the form of turnings, shavings, wool, and plates as opposed to fused iron or precipitated catalysts.

Classification of products: Boiling range at atmospheric temperature, ° C.:

Diesel oil..... 204 - 316

Heavy distillate..... 316 - 450

Wax..... > 450

C1 plus C2..... Includes methane, ethane, ethylene

C3..... Propane.

Anderson, R. B., Seligman, B., Shultz, J. F., Kelly, R., Elliott, M. A., Fischer-Tropsch Synthesis--Some Important Variables of the Synthesis on Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 391-397.

