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COBALT MOLYBDATE HYDROGENATION OF COKER DISTILLATE AND SHALE NAPHTHAS--INTERIM REPORT

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COBALT MOLYBDATE HYDROGENATION OF COKER DISTILLATE AND SHALE NAPHTHAS--INTERIM REPORT

by
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PREFACE

Hydrogenation offers one means of upgrading shale oil or shale-oil fractions for use in motor fuel production. Of particular interest in this field is the hydrogenation of coker distillates and shale naphthas produced by thermal cracking.

The purpose of this study was to determine the effects of variations in operating conditions upon yield, hydrogen consumption, and product quality. Based on the results of these surveys, optimum ranges of operating conditions were determined for each charge stock and catalyst life and heat of hydrogenation determined within these ranges.

APPARATUS AND EXPERIMENTAL PROCEDURE

A simplified diagram of the hydrogenation equipment used is shown in figure 1. The stainless-steel catalyst chamber was the fixed-bed type, equipped for downward flow, with an internal diameter of 1.25 inches and an internal length of 47.5 inches. A catalyst support placed 8 inches from the bottom provided a catalyst volume of 700 cc. Preheating of oil and hydrogen was achieved in a stainless-steel chamber mounted above the reactor and packed with quarter-mesh alundum grain. The condenser and receiver system also were of stainless construction.

Charge oil was stored in an electrically heated tank and was transferred to a burette for metering before being pumped by a piston-type pump to the preheater. Hydrogen obtained from standard shipping cylinders was metered through a rotameter and mixed with the oil at the inlet to the preheater.

Outlet gases were reduced to atmospheric pressure, metered through a positive displacement meter, and stored in a gas holder, from which samples were taken for mass-spectrometer analyses. As the gases were collected over water, ammonia and hydrogen sulfide were not reported except in isolated cases.

Catalyst volume was measured in a graduated cylinder, after tapping to assure uniform packing, and its weight determined before charging to the reactor. The system was purged of air by pressurizing several times with helium to approximately 100 p.s.i. and venting to the atmosphere. Before commencing a run, the system was brought to operating pressure with hydrogen gas.

During the run, product oil was continuously drained from the unit to maintain a nearly constant low level in the receivers. This was found

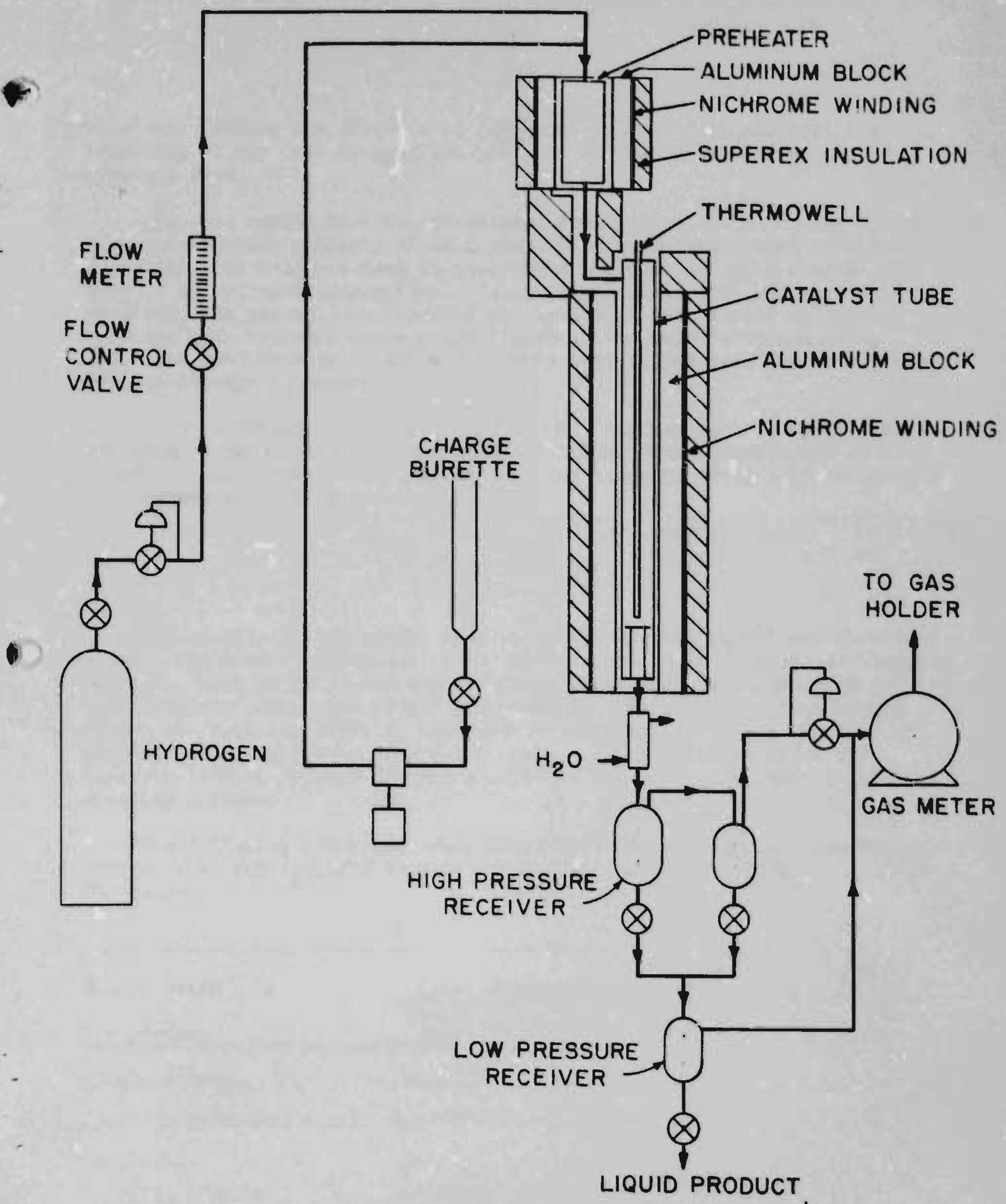

FIGURE 1.— FLOW DIAGRAM OF HYDROGENATION UNIT

necessary because the draw-off of any large volume of liquid from the receivers at one time dropped the pressure of the system and upset the hydrogen flow.

Hydrogen consumption was calculated from gas-volume measurements and mass spectrometer analysis of exit gas. This calculation took into consideration the hydrogen used to pressurize the unit and gave a true measure of hydrogen consumption. Calculations based upon hydrogen flow rate and exit gas volumes shown in the tables of this report will not give the true hydrogen consumption figures. The term "standard cubic feet" are used in this report means cubic feet of gas measured at 70° F. and one atmosphere pressure.

Used catalysts were cooled and weighed, and the gain in weight was reported as catalyst deposit or coke. Catalysts were regenerated in a separate furnace with air, the rate of flow being controlled to maintain the temperature within safe limits.

SUMMARY

The results of the survey runs contained in this report are discussed under three general headings: coker distillate, whole naphtha, and heavy naphtha. Each of these sections contains the optimum hydrogenation conditions for the production of the end products obtained from these charge stocks and contains over-all material balances that could be expected by producing these products from N-T-U crude. Information is given for catalyst life at or near optimum conditions when charging coker distillate or heavy naphtha.

The following tabulation summarizes the ranges of optimum conditions found. Data not included in this tabulation are those that have not been determined.

Charge stock	Coker distillate		Whole naphtha	Heavy naphtha
End product	Diesel fuel	Gasoline	Gasoline	Gasoline
Catalyst temp., °F.	825-850	950-980	960-980	950-980
Reaction pressure, p.s.i.	1000-1500	400-800	400 or more	600-800
L.H.S.V.	0.5-1.5	around 5.0		5.0-7.5
H_2 rate, SCF/bbl.	2000-4000-	* 2000		2000-3000
Vo/Vc	over 56			52.5 or up

HYDROGENATION OF COKER DISTILLATE

Introduction

In order to determine optimum operating conditions for hydrogenating coker distillate, one-hour runs were made over the temperature range 700° to 900° F., pressure range 500 to 1500 p.s.i., and hydrogen rates from 1,000 to 4,000 standard cubic feet per barrel. The space velocity was held constant at one volume of oil per volume of catalyst per hour in all runs.

Based upon the results of these survey runs, optimum conditions were selected and a 56-hour run was made to determine catalyst life and heat of hydrogenation; the plus-400° F. material from the 56-hour run was recycled in a later run to make Diesel fuel and jet fuel.

In addition to the runs in which the whole stock was hydrogenated, one run was made on the plus-260° F. material from coker distillate under conditions selected to produce gasoline when the naphtha which was formed during the run was recombined with the minus-260° F., non-hydrogenated material.

The coker distillate used for the hydrogenation studies was produced at Rifle in cracking run #10 under conditions which produced a 700° F. E. P. distillate.

Effect of Temperature

In table 1 are tabulated the process conditions, material balances, and liquid product properties for five runs on coker distillate. Except for differences in temperature, these runs were made under identical processing conditions. Gas analyses for these runs are given in table 2.

The effects of temperature on catalyst deposit and on sulfur and nitrogen content of the product are shown graphically in figure 2. Sulfur reduction was appreciable and approximately the same at all temperatures from 700° and 900° F. Nitrogen reduction increased with temperature, although for some unknown reason it was greater at 700° F. than at 800° F. However, as only one run was made at 700° F., little weight should be given to this nitrogen analysis.

As the furnace temperature was increased from 700° to 900° F., the catalyst deposit passed through a minimum around 825° F. This indicated that catalyst life would also be longest at this temperature, other operating conditions being the same.

Table 1.—Temperature survey of CoMoO$_4$ hydrogenation of coker distillate.

	Charge	Cat. run #101	Cat. run #102	Cat. run #106	Cat. run #105	Cat. run #103
Process conditions:						
Temperature, furnace, °F.		700	800	825	850	900
Pressure, p.s.i.		1000	1000	1000	1000	1000
L.H.S.V.		1.0	1.0	1.0	1.0	1.0
Vo/Vc		1:1	1:1	1:1	1:1	1:1
Hydrogen flow, scf./bbl.		2000	2000	2000	2000	2000
Hydrogen consumed, scf./bbl.		577	776	932	1019	1507
Effluent gas, scf./bbl.		1598	1355	1186	1095	1214
Cat. deposit, wt. % cat.		9.4	7.1	6.6	7.3	6.7
Material balances:						
Liquid product, vol. %		91.0	93.9	90.0	90.8	81.6
" " wt. %		87.1	88.4	84.3	84.3	74.7
Coke, wt. %		8.2	6.3	5.6	6.0	5.9
Water, wt. %		1.6	2.1	2.2	1.8	2.3
Gas + loss, wt. %		3.1	3.2	7.9	7.9	17.1
Liquid product inspections:						
Gravity, °API	33.8	41.2	44.0	45.0	46.6	49.0
A.S.T.M. dist., °F.						
IBP	123	133	148	143	127	125
10	260	215	243	230	215	179
50	492	403	433	408	396	313
90	629	571	598	565	563	506
EP	681	655	663	655	657	598
Rec., vol. %	97.0	97.5	97.0	97.0	97.0	96.0
Res., vol. %	1.0	1.0	1.0	1.1	1.1	1.8
Loss, " "	2.0	1.5	2.0	1.9	1.9	2.2
Sulfur, wt. %	0.63	0.05	0.03	0.03	0.06	0.02
Nitrogen," "	1.43	0.21	0.28	0.25	0.21	0.08
Viscosity, Kin., 70° F.	3.10	2.20	1.78	1.48	1.16	0.95
" " 100° F.	2.19	1.14	1.38	1.36	1.10	0.87
Pour point, °F.	10	-15	3	-8	-18	-65
Naphtha, 400° F. E.P., vol.% Coker distillate[1]	26.5	44.6	38.1	43.0	46.4	58.2

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[1] Estimated from A.S.T.M. distillation.

Table 2.—Gas analyses, temperature survey, $CoMoO_4$ hydrogenation of coker distillate.

	Cat. run #101	Cat. run #102	Cat. run #106	Cat. run #105	Cat. run #103
Process conditions:					
Temperature, furnace, °F.	700	800	825	850	900
Pressure, p.s.i.	1000	1000	1000	1000	1000
L.H.S.V.	1.0	1.0	1.0	1.0	1.0
Vo/Vc	1.0	1.0	1.0	1.0	1.0
Hydrogen flow, scf./bbl.	2000	2000	2000	2000	2000
Hydrogen consumed, scf./bbl.	577	776	932	1019	1507
Effluent gas, scf./bbl.	1598	1355	1186	1095	1214
Gas analyses:					
Hydrogen	97.7	91.3	68.1	80.5	59.7
Methane	0.7	5.1	17.4	12.0	21.0
Ethane	0.5	0.8	7.8	4.2	7.4
Propane	0.4	1.7	3.4	1.8	3.6
Butanes	0.4	0.1	2.5	1.0	1.2
Pentanes					0.7
Ethene		0.7			0.1
Propene	0.1	0.3	0.6	0.3	
Butenes	0.1				0.5
Pentenes					0.4
Benzene					1.1
Toluene					0.1
Carbon dioxide	0.1		0.3	0.3	1.0
Carbon monoxide					3.0
Total	100.0	100.0	100.1	100.1	99.8
Avg. molecular weight	2.5	4.0	9.8	6.4	12.4

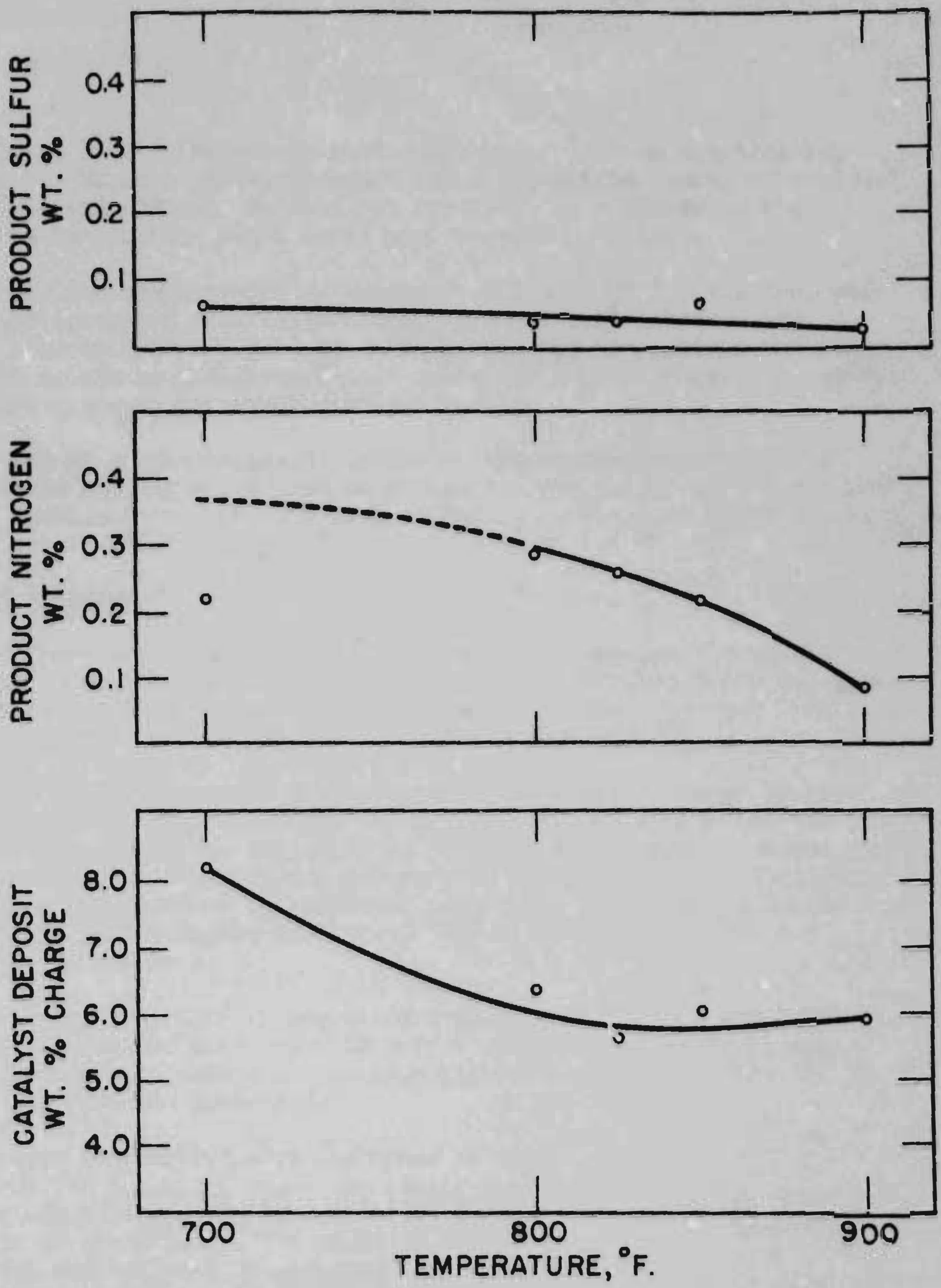

FIGURE 2-HYDROGENATION OF COKER DISTILLATE

Catalyst-Cobalt Molybdate
Pressure - 1000 p. s. i.
L. H. S. V. - 1.0
V_0 / V_c - 1.0
Hydrogen Rate - 2000 scf/bbl.

Yield of liquid product dropped sharply at reaction temperatures over 850° F. Naphtha yield, based on coker distillate increased rapidly between 850° and 900° F. No data are available to indicate at what temperature the naphtha yield would pass through a maximum.

At reaction temperatures up to and including 900° F., the hydrogen consumption increased with temperature. The greatest increase was detected between 850° and 900° F. Here again, the temperature was not taken high enough to indicate at what point the dehydrogenation reactions would cause hydrogen consumption to decrease.

The volume of gas produced was low at temperatures up to 850° F. but increased rapidly above this temperature. The weight of gas produced, however, continuously increased with temperature; the most rapid increase occurred between 850° and 900° F.

Effect of Pressure

Data from three runs which show the effect of pressure upon the hydrogenation of coker distillate are presented in tables 3 and 4. These were made at the same temperature, space velocity, and hydrogen flow rate while the pressure was varied between 500 and 1500 p.s.i.

The effect of increased pressure upon sulfur and nitrogen content of the product is quite apparent. At 1500 p.s.i. the sulfur content was reduced almost to the vanishing point while the nitrogen content was only one-half that at a reaction pressure of 500 p.s.i. The catalyst deposit also decreased as the pressure increased, indicating a longer catalyst life at the higher pressures. The effects of pressure are illustrated in figure 3.

Liquid product recovery increased rapidly between 1000 and 1500 p.s.i., while naphtha production increased continuously with pressure. A slight increase in volume of the hydrogen-free gas was noticed as the reaction pressure was increased.

Hydrogen consumption also increased rapidly as the pressure was raised from 500 to 1500 p.s.i. The higher hydrogen consumption and the lower specific gravity of the liquid product indicate a higher percentage of paraffins in the products at the more elevated pressures. These data, and analyses of products from hydrogenation of other shale-oil fractions, indicate that high pressures have a deleterious effect upon octane ratings.

Effect of Hydrogen Rate

Tables 5 and 6 list processing conditions and product properties of four typical runs which show the effect of varying hydrogen rate when hydrogenating coker distillate.

Table 3.--Pressure survey, $CoMoO_4$ hydrogenation of coker distillate.

	Charge	Cat. run #104	Cat. run #106	Cat. run #99
Process conditions:				
Length of run, hrs.		1	1	1
Temperature, furnace, °F.		825	825	825
Pressure, p.s.i.		500	1000	1500
L.H.S.V.		1.0	1.0	1.0
Vo/Vc		1.0	1.0	1.0
Hydrogen flow, scf./bbl.		2000	2000	2000
Hydrogen consumed, scf./bbl.		683	932	1000
Effluent gas, scf./bbl.		1361	1186	1185
Cat. deposit, wt. % cat.		7.7	6.6	5.2
Material balances:				
Liquid product, vol. %		92.8	90.0	94.1
" " wt. %		87.8	84.3	87.6
Coke, wt. %		6.6	5.6	4.6
Water, wt. %		1.6	2.2	2.4
Gas + loss, wt. %		4.0	7.9	5.4
Liquid product inspections:				
Gravity, °API.	33.8	43.2	45.0	46.1
Sp. gr., 60/60° F.	0.8561	0.8098	0.8019	0.7969
A.S.T.M. dist., °F. at 760				
IBP	123	137	143	154
5 evap.	219	164	199	205
10 "	260	233	230	227
20 "	353	280	282	274
30 "	425	347	329	323
40 "	459	386	374	370
50 "	492	423	408	408
60 "	521	457	437	445
70 "	553	490	479	481
80 "	588	527	519	521
90 "	629	577	565	581
95 "	679	629	623	635
EP	681	645	655	675
Rec., vol. %	97.0	97.0	97.0	97.0
Res., vol. %	1.0	1.1	1.1	1.2
Loss, vol. %	2.0	1.9	1.9	1.8
Sulfur, weight percent	0.63	0.04	0.03	0.01
Nitrogen, " "	1.43	0.35	0.25	0.18
Viscosity, kinematic, 70° F.	3.10	1.66	1.48	1.50
100° F.	2.19	1.29	1.36	1.18
Pour point, °F.	10	-9	-8	2
Naphtha, 400° F. E.P., Vol. % Coker distillate[1]	26.5	40.6	43.0	45.1

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[1] Estimated from A.S.T.M. distillation.

Table 4.--Pressure survey, gas analyses, $CoMoO_4$ hydrogenation of coker distillate.

	Cat. run #104	Cat. run #106	Cat. run #99
Process conditions:			
Temperature, furnace, °F.	825	825	825
Pressure, p.s.i.	500	1000	1500
L.H.S.V.	1.0	1.0	1.0
Vo/Vc	1.0	1.0	1.0
Hydrogen flow, scf./bbl.	2000	2000	2000
Hydrogen consumed, scf./bbl.	683	932	1000
Effluent gas, scf./bbl.	1361	1186	1185
Gas analyses:			
Hydrogen	87.1	68.1	86.3
Methane	6.4	17.4	8.5
Ethane	3.2	7.8	2.8
Propane	1.7	3.4	1.1
Butanes	0.9	2.5	0.4
Ethene	Tr.	--	0.1
Propene	0.1	0.6	0.1
Butene	0.1	--	0.1
Carbon dioxide	Tr.	0.3	0.1
Carbon monoxide	--	--	0.4
Nitrogen	0.4	--	0.1
Total	99.9	100.1	100.0
Avg. molecular weight	5.2	9.8	5.0

Table 5.--Hydrogen rate survey, CoMoO$_4$ hydrogenation of coker distillate

	Charge	Cat Run #127	Cat Run #106	Cat Run #126	Cat Run #131
Process conditions:					
Length of run, hrs.		1	1	1	1
Temperature, furnace, °F.		825	825	825	825
Pressure, p.s.i.		1000	1000	1000	1000
L.H.S.V.		1.0	1.0	1.0	1.0
Vo/Vc		1.0	1.0	1.0	1.0
Hydrogen flow, scf./bbl.		1000	2000	3000	4000
Hydrogen consumed, scf./bbl.		1099	932	1225	1573
Effluent gas, scf./bbl.		524	1186	1955	2925
Cat. deposit, wt. % cat.		6.5	6.6	5.0	4.6
Material balances:					
Liquid product, vol. %		88.7	90.0	92.1	95.0
Liquid product, wt. %		84.2	84.3	85.7	88.5
Coke, wt. %		5.7	5.6	4.4	4.2
Water, wt. %		1.8	2.2	1.9	7.7
Gas + loss, wt. %		8.3	7.9	7.9	4.5
Liquid product inspections:					
Gravity, °API	33.8	42.6	45.0	46.1	46.0
Sp. gr., 60/60° F.	0.8561	0.8130	0.8019	0.7967	0.7973
A.S.T.M. dist., °F at 760					
IBP	123	142	143	134	122
5	219	207	199	179	178
10	260	236	230	212	228
20	353	275	282	269	275
30	425	330	329	314	324
40	459	375	374	364	356
50	492	413	408	405	402
60	521	450	437	439	442
70	553	464	479	474	479
80	588	497	519	517	506
90	629	513	565	524	569
95	679	----	623	594	613
EP	681	514	655	594	623
Rec., vol. %	97.0	91.0	97.0	96.0	97.0
Res., vol. %	1.0	7.0	1.1	2.0	1.5
Loss, vol. %	2.0	2.0	1.9	2.0	1.5
Sulfur, wt. %	0.63	0.05	0.03	0.01	0.01
Nitrogen, wt. %	1.43	0.55	0.25	0.15	0.10
Viscosity, kin., 70° F.	3.10		1.48		
Viscosity, kin., 100° F.	2.19		1.36		
Pour point, °F.	10		-8		
Naphtha, 400° F. EP, vol. % Coker distillate1/	26.5	41.4	43.0	44.9	47.1

1/ Estimated from A.S.T.M. distillation.

Table 6.--Gas analyses, hydrogen rate survey, $CoMoO_4$ hydrogenation of coker distillate

	Cat Run #127	Cat Run #106	Cat Run #126	Cat Run #131
Process conditions:				
Temperature, furnace, °F.	825	825	825	825
Pressure, p.s.i.	1000	1000	1000	1000
L.H.S.V.	1.0	1.0	1.0	1.0
Vo/Vc	1.0	1.0	1.0	1.0
Hydrogen flow, scf./bbl.	1000	2000	3000	4000
Hydrogen consumed, scf./bbl.	1099	932	1225	1573
Effluent gas, scf./bbl.	524	1186	1955	2925
Gas analyses:				
Hydrogen	76.4	68.1	86.3	89.7
Methane	11.0	17.4	6.2	3.9
Ethane	6.0	7.8	4.1	2.9
Propane	2.9	3.4	1.6	1.9
Butanes	1.3	2.5	0.5	0.8
Pentanes	0.9		0.3	
Ethene	0.2		0.1	
Propene	0.3	0.6		
Butenes	0.2		0.1	0.1
Pentenes	0.2		0.2	
Carbon dioxide	0.3	0.3	0.1	0.1
Carbon monoxide	0.3			0.4
Ammonia			0.5	
Total	100.0	100.1	100.0	99.8
Avg. molecular weight	8.3	9.8	5.5	4.8

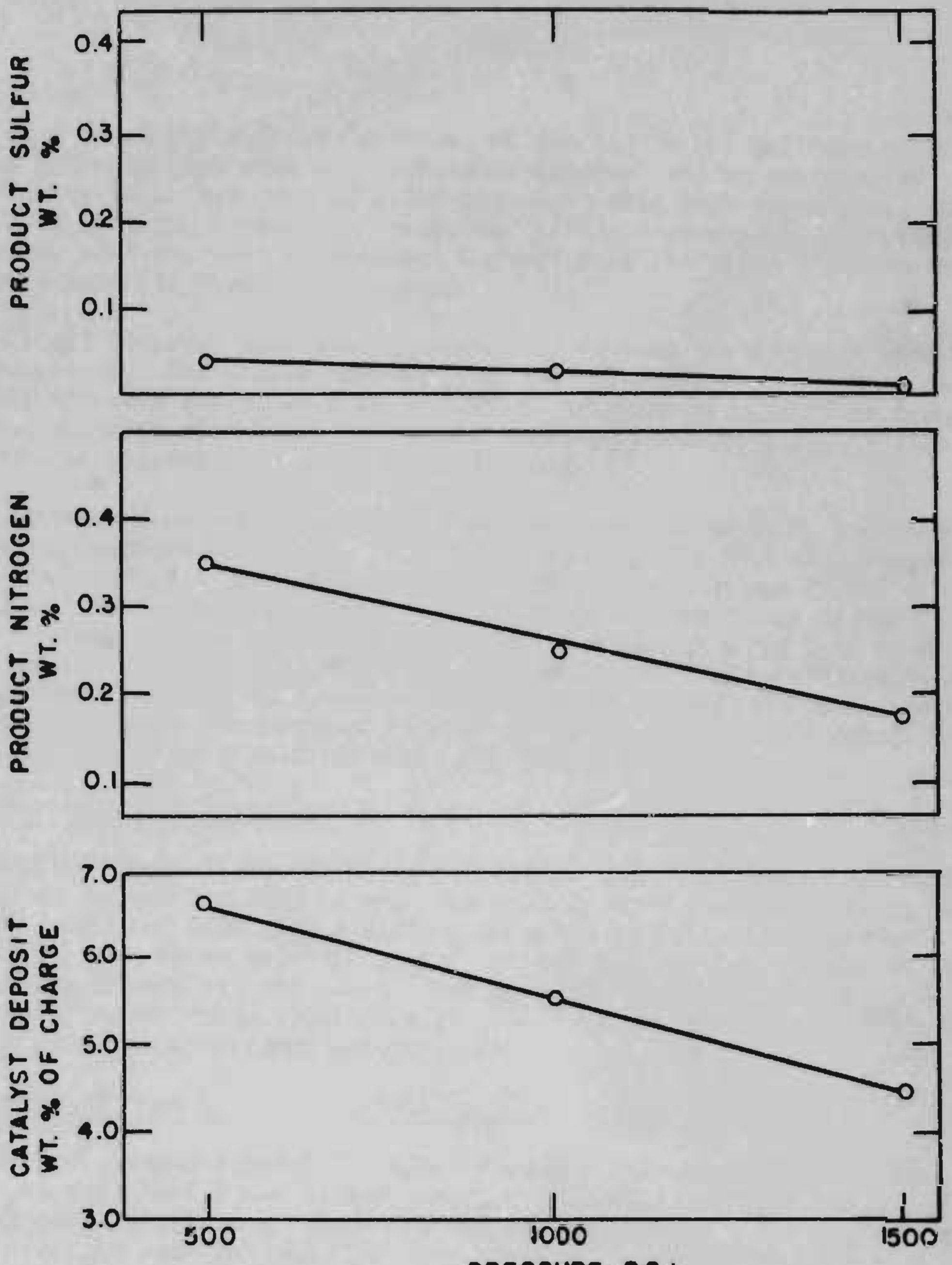

FIGURE 3.-HYDROGENATION OF COKER DISTILLATE

Catalyst—Cobalt Molybdate
Temperature—825 °F.
L.H.S.V.—1.0
Vo / Vc—1.0
H_2 Rate—2000 SCF / bbl.

Sulfur and the nitrogen contents of the liquid product were reduced as the hydrogen flow rate was increased, although sulfur was removed effectively at a flow rate of 3,000 standard cubic feet per barrel. The effect of hydrogen rates upon sulfur and nitrogen removal is depicted in figure 4. The decrease of catalyst deposit with increased hydrogen rates is shown in table 5 and in figure 4.

Liquid recovery and naphtha production rose as the hydrogen rate was increased. The higher partial pressures of hydrogen that exist at the higher rates result in a lower partial pressure of oil. This probably reduces cracking of the oil to gas and coke and produces a higher liquid recovery as suggested by other investigators.[1]

Hydrogen consumption in these runs, as shown in table 5, does not completely conform to theory. Run 106 at 2,000 cubic feet of hydrogen per barrel showed a lower hydrogen consumption than did run 127 with only 1,000 cubic feet of hydrogen. Because of the shortness of the run (one hour) a small error in the hydrogen analysis could lead to a large error in hydrogen consumption. A longer run (56 hours) that will be discussed later in this report was made under identical conditions as run 106. Hydrogen consumption in this run was 1,333 standard cubic feet per barrel, more in agreement with data from other runs.

Effect of Space Velocity

The effect of different space velocities upon the hydrogen of coker distillate is not too well known. Preliminary work (not included in this report) indicated that little difference could be detected in product properties when space velocity ranged between 0.5 and 1.5 volumes of oil per volume of catalyst per hour. Work on shale naphthas, however, has shown that higher space velocities (5.0 to 7.5) are optimum for production of gasoline of satisfactory octane rating.

Production of Diesel Fuel, Jet Fuel, and Low Octane Gasoline

Figure 5 shows a possible refining scheme for production of Diesel fuel, jet fuel, and a low octane gasoline by cobalt molybdate hydrogenation of coker distillate. This diagram includes yields of all products as obtained in runs 113 and 119.

The conditions used for all processing operations in this scheme are given in table 7. Optimum conditions of temperature and pressure were chosen from the surveys discussed previously. Hydrogen rates for runs 113 and 119 were lower than optimum because of a temporary shortage of hydrogen. However, the rate used (2,000 standard cubic feet per barrel) was sufficient to give satisfactory results.

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[1] Cole, R. M., and Davidson, D. D., Ind. Eng. Chem., 41, 2711 (1949).

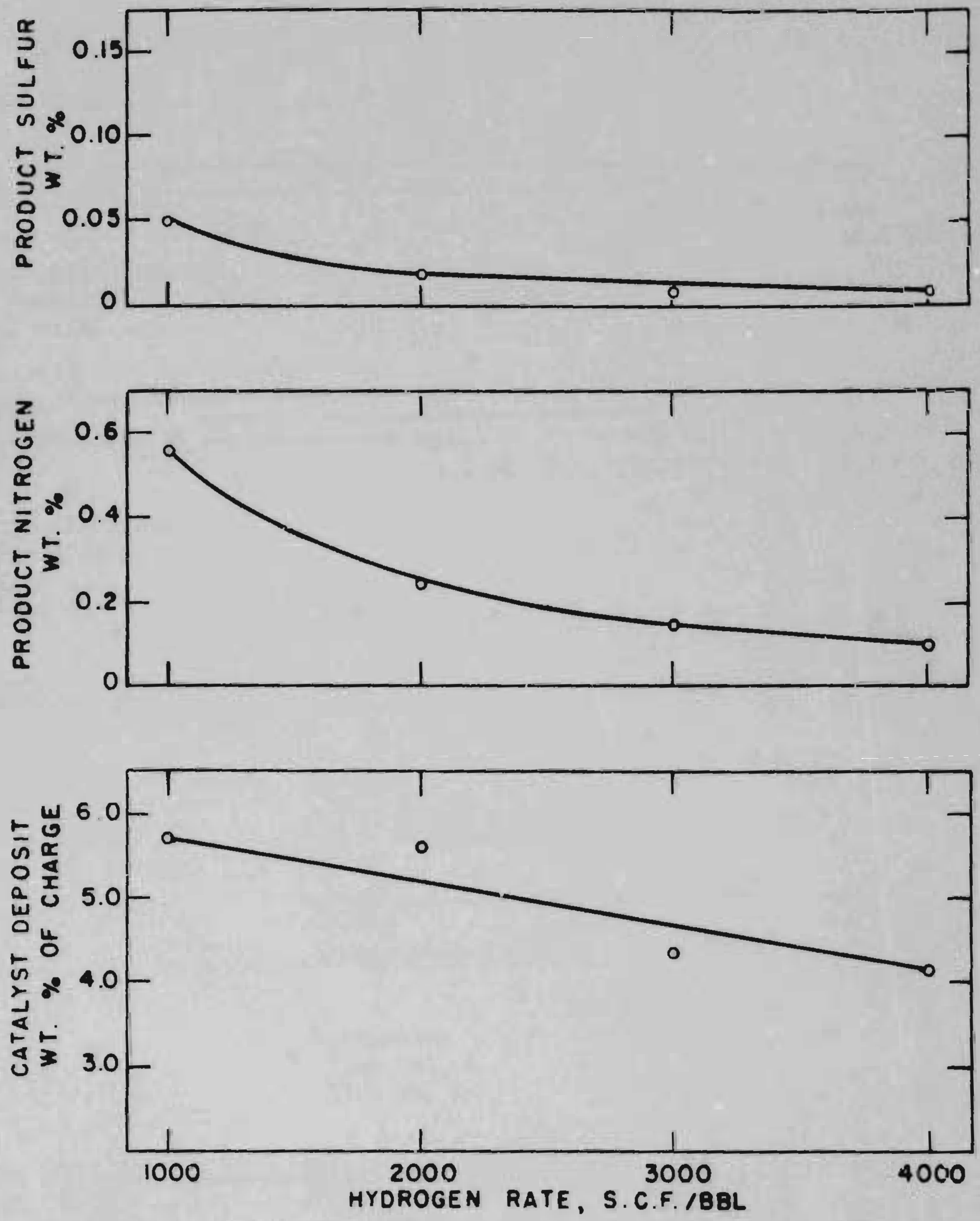

FIGURE 4.-HYDROGENATION OF COKER DISTILLATE

Catalyst-Cobalt Molybdate

Temperature-825 °F.

Pressure — 1000 °F.

L.H.S.V. — 1.0

Vo/Vc — 1.0

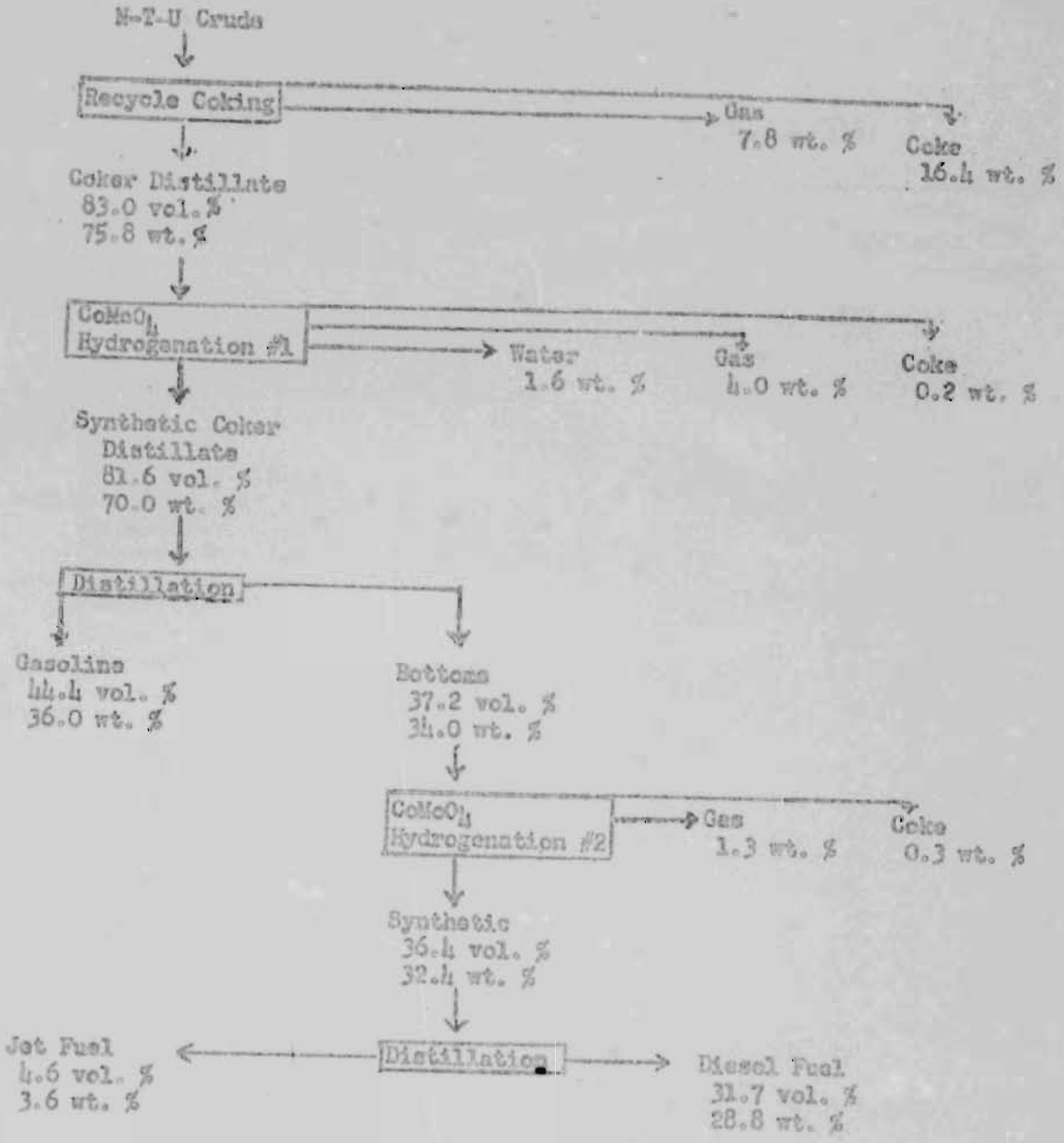

Figure 5.--CoMoO$_4$ Hydrogenation of Coker Distillate

Table 7.--Process conditions, Cat Run #113 & #119.

Process	Recycle coking	$CoMoO_4$ hydrogenation #1	 #2
Run. no.	10	113	119
Charge rate, shale oil, bbl./stream day	86.3		
" " , recycle stock, " " "	212.8		
Recycle ratio, recycle to fresh feed	2.5		
Heater inlet			
Temp., °F.	437		
Pressure, p.s.i.g.	340		
Heater outlet			
Temp., °F.	940		
Pressure, p.s.i.g.	60		
Reaction or coke chamber			
Temperature, °F.	825	1/825	2/825
Pressure, p.s.i.g		1000	1000
Flash chamber			
Temperature, top, °F.	780		
Fractionator			
Temperature, top, °F.	360		
Temperature, bottom, °F.	600		
Pressure, bottom, p.s.i.g.	5		
L.H.S.V.		1.0	1.0
Vo/Vc		56	3.0
Hydrogen rate, scf/bbl.		2000	2000
Time on stream, cat., hrs.		56	3
Cat. deposit, wt. % catalyst		14.3	2.9
Hydrogen consumption, scf/bbl.		1333	--

1/ Maximum reaction temperature varied between 835° and 865° F.

2/ Maximum reaction temperature was 3 to 5 degrees higher than furnace temperature.

Analyses of the liquid products shown in figure 5 are given in table 8. No analysis of the total liquid product was made.

The Diesel fuel made by the second pass hydrogenation meets specifications for a fuel of high pour point. Because of the low sulfur content of this fuel, it could be utilized for blending with a Diesel fuel containing more than specification sulfur. The carbon residue of this Diesel fuel was higher than allowed by some specifications. This can be adjusted partially by lowering the end point.

Analysis reported for jet fuel was determined on the 432° F. E.P. distillate obtained from the hydrogenation of the recycle stock. While the properties are incomplete, they lie within specification limits and agree very well with those reported for other shale jet fuels.2/3/

A large portion of the material shown as gasoline in the first pass operation could be marketed as jet fuel. Its low sulfur and high paraffin content are desirable properties in a jet fuel blending stock.

As expected, the gasoline produced by hydrogenating at moderate temperatures and high pressures had a low clear octane number. The lead response, however, was very good. Three milliliters of lead were sufficient to raise the octane number close to specifications for regular grade gasoline. Although research octane numbers were not determined, the low olefin content of the gasoline precludes a good octane sensitivity. Sulfur and nitrogen contents of this gasoline were very low, the low sulfur content aiding the lead response of the gasoline.

When this low octane gasoline was reformed over chrome-alumina to a 91.3 percent yield, the unleaded octane number rose to 62 and with three milliliters of lead the octane was 79.1.4/

Analyses of gases from all the processing operations used in this refining scheme are given in table 9. The analyses for the 56-hour run were made on spot samples taken at various times throughout the run, and remained essentially uniform throughout. This uniformity, coupled with the low olefinic content of the gases even after 56 hours indicated that the catalyst was still active at the end of this period.

Catalyst Life

The 56-hour run described previously was used to obtain information on the catalyst life of cobalt molybdate when hydrogenating coker distillate.

2/ Progress Report, Union Oil Company, Jan. 5, 1949.

3/ Bur. of Mines, Rept. of Invest. 4771, 1950.

4/ Carpenter, H. C., and Hopkins, C. B., Shale-Oil Refining Research, Pet. 423-3, U. S. Bur. of Mines, Laramie Station Project Report, March, 1950.

Table 8.--Liquid product analyses, Cat Run #113 & #119.

Type product	Coker distillate	Gasoline	Bottoms	Jet Fuel	Diesel Fuel
N-T-U crude, vol. percent	83.0	44.4	37.2	4.6	31.7
Gravity, °API	33.8	55.6	34.3	48.3	35.8
Sp. Gr., 60/60° F.	0.8561	0.7565	0.8535	0.7869	0.8456
A.S.T.M. dist., °F. at 760					
IBP	123	138	441	122	430
10	260	195	469	192	460
50	492	292	509	335	501
90	629	371	---	414	602
EP	681	396	---	432	644
Rec., vol. percent	97.0	98.0	---	96.0	98.0
Res., vol. "	1.0	1.0	---	1.0	1.0
Loss, " "	2.0	1.0	---	3.0	1.0
Sulfur, wt. percent	0.63	[1]0.01	0.01	0.01	nil
Nitrogen," "	1.43	[1]0.04	0.29	0.04	0.02
Tar acids, vol. percent		nil			
Tar bases, " "		<0.1			
Par. + naph. " "		84			
Olefins, " "		2			
Aromatics, " "		14			
Octane, motor, clear		46			
+1 ml. TEL		61			
+3 ml. TEL		73			
Carbon residue, rams. 10%			0.41		0.20
" " , whole oil	1.01				0.03
Cetane No.	25		41		51.5
Aniline point, °F.	89		144		146
Flash point, °F., P.M.			226		225
Pour point, °F.	10		25		20
Viscosity, Kin., at 70° F.	3.10				3.87
100° F.	2.19		2.90		2.75
210° F.			1.17		
C/H ratio					6.74

---

[1] Washed with 1% H_2SO_4 and 1% NaOH.

Table 9.--Gas analyses, Cat Run #113 & Cat Run #119.

Source	Recycle delayed coking	CoMoO$_4$ Hydrogenation #1							CoMoO$_4$ hydrogen. #2
Time sample taken, hrs.	entire	6	14	23	29	46	52	56	entire
Analyses, mole percent									
Hydrogen	11.1	70.8	60.4	75.5	72.4	76.6	80.7	77.7	80.4
Methane	42.5	14.1	17.7	13.2	12.9	11.7	9.3	12.5	9.3
Ethane	13.0	7.4	8.0	6.7	6.7	6.8	4.9	4.7	4.1
Propane	6.1	4.7	4.6	3.0	4.7	3.0	3.2	2.5	2.1
Butanes	4.1	1.5	1.9	1.1	1.7	0.9	1.6	1.8	
Pentanes	1.9	0.5	0.5	—	0.5	0.1	—		
Hexanes	0.4	—	—	—	—	—			
Ethene	2.7	—	0.1						1.0
Propene	5.2	—	—						1.0
Butenes	3.5	0.1	0.4	0.2	0.2	0.2	0.2	0.3	1.0
Pentenes	3.1	0.1	—		0.2	0.1			
Hexenes	1.0	—	—						
Heptenes	0.1	—	—						
Carbon dioxide	0.7	0.1	0.2	0.2	0.1	0.2		0.4	1.0
Carbon monoxide	1.7	—	1.0			0.3			
Nitrogen	0.7	0.6	5.2		0.5		0.1		
Hydrogen sulfide	2.1	—	—						
Total	99.9	99.9	100.0	99.9	99.9	99.9	100.0	99.9	99.9
Avg. molecular weight	27.4	9.8	11.7	7.8	9.4	7.7	7.0	7.4	7.0

Liquid product samples were collected periodically and analyzed for sulfur and nitrogen as a means of determining catalyst deterioration. Listed below are the results of some of these tests.

Throughout, Vo/Vc[5]	S wt. percent	N wt. percent
charge	0.63	1.43
2	----	0.09
4	0.08	0.08
6	0.04	0.11
8	0.01	0.14
24	0.01	0.15
56	0.01	0.14

Analyses of periodic samples of hydrogenated coker distillate during the 56-hour run show that over 98 percent of the sulfur was being removed from the oil at the end of this period. Nitrogen content of the product increased slightly during the first four hours of operation but leveled off thereafter, and 90 percent of the nitrogen was removed from the sample taken at the end of 56 hours.

These results combined with the gas analyses obtained for this same run indicate that under the conditions used (i.e., temperature, 825° F.; pressure, 1000 p.s.i.; hydrogen rate, 2000 SCF/bbl.; L.H.S.V., 1.0) the catalyst life for hydrogenating coker distillate is in excess of 56 hours. It is known from the survey runs that the use of higher pressures and hydrogen rates would probably increase the catalyst life.

Production of Regular-Grade Gasoline

An alternate method for producing gasoline from coker distillate is shown in figure 6. In this scheme, the light naphtha, boiling below 260° F., and containing a considerable amount of olefins was separated by distillation and caustic washed to remove dissolved hydrogen sulfide. The plus-260° F. material was hydrogenated at high temperature and moderate pressure to produce a heavy gasoline having relatively high octane compared with the gasoline produced previously from coker distillate. Operating conditions for this hydrogenation are included in table 10.

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[5] L.H.S.V. = 1.0.

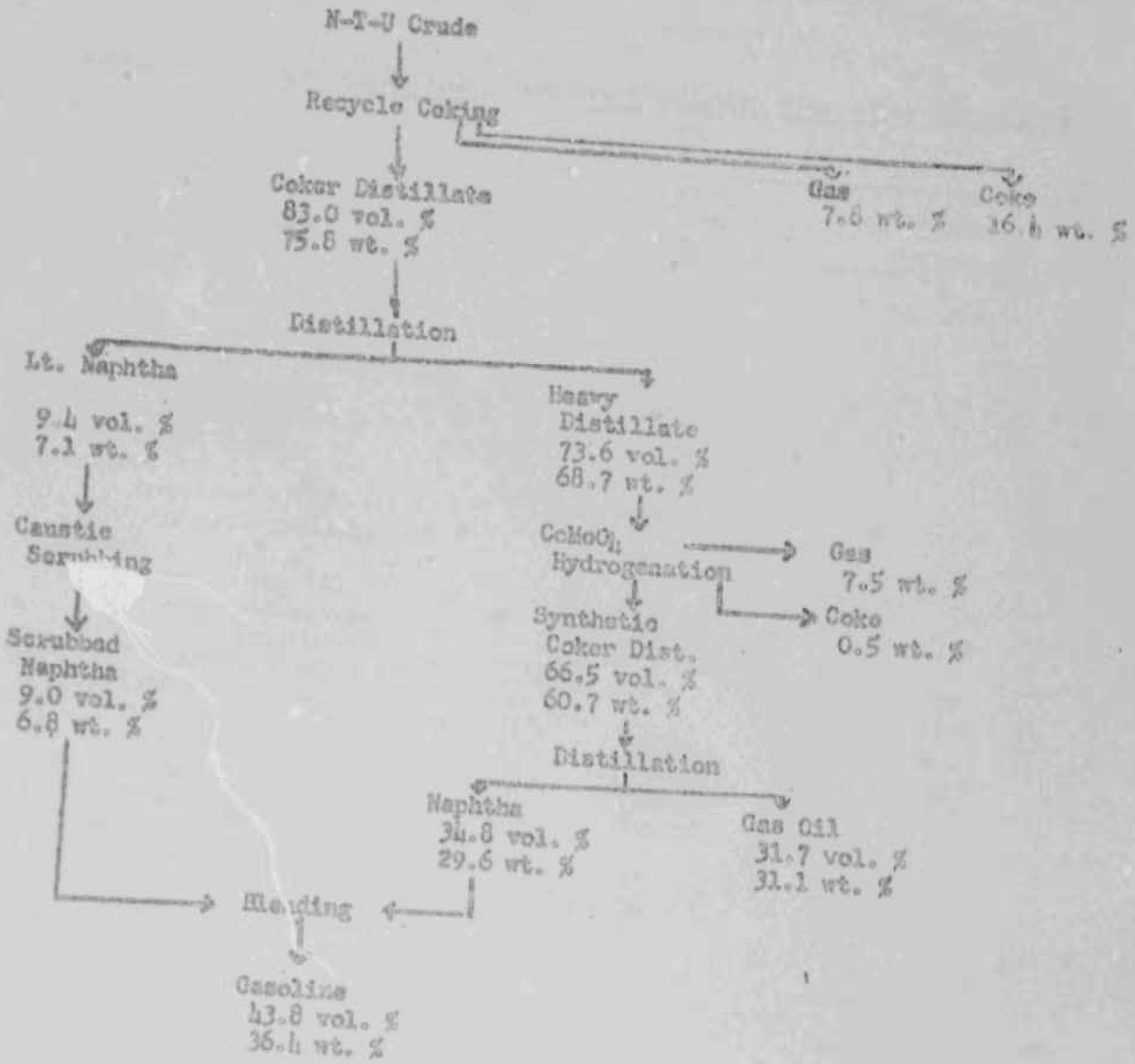

Figure 6.--Material Balances, Cat. Run #209[1/]

[1/] No loss basis.

Table 10.--Process conditions, gasoline production from coker distillate

Process	Recycle Delayed Coking	$CoMoO_4$ Hydrogenation
Run number	10	209
Charge rate, shale oil, bbl/stream day	86.3	
Charge rate, recycle stock, bbl/stream day	212.8	
Recycle ratio, recycle to fresh feed	2.5	
Heater, inlet		
Temperature, °F.	437	
Pressure, p.s.i.g.	340	
Heater, outlet		
Temperature, °F.	940	
Pressure, p.s.i.g.	60	
Reaction or coke chamber		
Temperature, avg., °F.	825	958
Temperature, max., °F.		967
Temperature, furnace, °F.		900
Pressure, p.s.i.g.		410-415
Flash chamber		
Temperature, top, °F.	780	
Fractionator		
Temperature, top, °F.	360	
Temperature, bottom, °F.	600	
Pressure, bottom, p.s.i.g.	5	
L.H.S.V.		5.0
Vo/Vc		20
Hydrogen rate, scf/bbl.		2000
Time on stream, cat., hrs.		4
Cat. deposit, wt. % catalyst		16.4

The gasoline produced by hydrogenation was blended with the scrubbed light gasoline. In table 11 are listed product analyses for most of the intermediate products and all liquid end products. Analyses of the effluent gases produced during recycle delayed coking and hydrogenation are given in table 12.

Data given in table 11 show that considerable amounts of sulfur were removed from the light naphtha by caustic scrubbing. While a large portion of this undoubtedly was present as hydrogen sulfide, some of the lower molecular weight mercaptans also were removed. The volume of gasoline lost by this treating step, however, was negligible.

The gasoline produced by hydrogenation of the heavy distillate met all requirements for regular grade gasoline except gum, and use of inhibitors would alleviate this problem. The blend, although of a slightly poorer quality, also met requirements except for gum. The advantage of blending, in spite of the lower quality product, lies in an increased yield of refined gasoline and in a gasoline with better octane sensitivity.

Complete analytical data are not available for the hydrogenated gas oil. Available data indicate that this gas oil could be used as a low quality Diesel fuel or as a charge stock to other refining processes.

The run used as a basis for this type of hydrogenation scheme was intended primarily as a survey run. The results obtained represent the only data available for this type of operation. It is probable, however, that a higher octane gasoline could be produced by the use of better hydrogenating conditions and a better quality light naphtha for blend stock.

Conclusions

Data shown in the previous tables are sufficient to indicate the effects of temperature, pressure, and hydrogen rate upon hydrogenation of coker distillate.

These effects are:

1. As the reaction temperature is increased between 700° and 900° F.:

    a. Sulfur reduction is appreciable at all temperatures.
    b. Nitrogen reduction increases with temperature.
    c. Catalyst deposit passes through a minimum at 825° F.
    d. Yield of liquid product is fairly uniform from 700° to 850° F. but decreases rapidly thereafter.

Table 11.--Liquid product analyses, gasoline production from coker distillate

Type product	Coker distillate	Light naphtha	Scrubbed naphtha	Heavy distillate	Heavy naphtha	Gas oil	Blended gasoline
Sample #RRS	50-45	51-806	51-816	51-807	51-825	51-832	51-826
Sp. Gr. 60/60° F.	0.8576	0.7109	0.7202	0.8767	0.7808	0.9079	0.7619
Gravity, °API	33.5	67.6	67.7	29.9	49.7	24.4	54.2
ASTM Dist., °F, at 760							
IBP	123	115	108	277	110	—	105
10%	260	136	140	349	187	—	161
50%	492	195	197	492	317	—	283
90%	629	246	245	638	384	—	381
EP	681	261	263	666	420	—	419
Rec. vol. percent	97.0	96.5	96.0	97.0	98.0	—	97.5
Res, " "	1.0	1.5	1.0	2.5	0.6	—	0.5
Loss " "	2.0	2.0	3.0	0.5	1.4	—	2.0
Octane, F-2, motor, clear	—	—	68.1	—	66.2	—	66.7
+1 ml. TEL	—	—	71.0	—	71.8	—	72.1
+3 ml. TEL	—	—	73.4	—	76.2	—	75.9
Octane, F-1, research, clear	—	—	76.6	—	72.4	—	74.1
+1 ml. TEL	—	—	79.6	—	—	—	—
+3 ml. TEL	—	—	82.7	—	—	—	84.3
Hydrocarbon type, vol. %							
Paraffins	—	—	34	—	51	—	45
Naphthenes	—	—	3	—	0	—	3
Olefins	—	—	57	—	22	—	30
Aromatics	—	—	6	—	27	—	22
Tar acids, vol. %	—	—	0.0	—	0.7	—	0.9
Tar bases, vol. %	—	—	0.8	—	10.1	—	7.3
A.S.T.M. Gum, mg./100 ml.	—	—	30.9	—	20.4	—	33.6
Cu. Dish " " " "	—	—	51.0	—	325	—	293
Induction period, hrs.	—	—	22.08	—	24+	—	24+
Doctor	—	—	Sweet	—	Sweet	—	Sweet
Corrosion	—	—	Neg.	—	Pos.	—	Pos.
Sulfur, wt. percent	0.63	0.44	0.30	0.71	0.12	0.29	0.16
Nitrogen, " ", raw	1.43	0.20	0.13	1.86	1.18	1.88	0.94
" " ", water washed	—	—	—	—	1.04	—	0.84
R.V.P.							insufficient sample
Pour point, °F.	10	—	—	15	—	—	—
Viscosity, kin, 70° F.	3.10	—	—	4.27	—		—
" , kin, 100° F.	2.19	—	—	2.91	—		—
Aniline point, °F.	—	—	—	—	—	176	—
Diesel index	—	—	—	—	—	42.9	—

Table 12.--Gas analyses, gasoline production from coker distillate

Source	Recycle Delayed Coking	$CoMoO_4$ Hydrogenation
Hydrogen	11.1	72.5
Methane	42.5	11.1
Ethane	13.0	7.7
Propane	6.1	5.0
n-butane	4.1	2.0
i-butane		
n-pentane	1.9	
i-pentane		
Hexanes	0.4	
Ethylene	2.7	
Propylene	5.2	0.5
Butene-1	3.5	0.7
Butene-2		
i-butene		
Pentenes	3.1	
Hexenes	1.0	
Heptenes	0.1	
Ammonia	----	
Nitrogen	0.7	
Carbon Dioxide	0.7	
Carbon Monoxide	1.7	0.5
Hydrogen Sulfide	2.1	
Molecular weight	27.4	9.6

e. Naphtha yield increases rapidly between 850° and 900° F.
f. Hydrogen consumption varies with temperature with the greatest increase occurring between 850° and 900° F.
g. Volume of reaction gases is low at temperatures below 850° F. but increases rapidly at higher temperatures. The weight of reaction gases increases continuously with increasing temperature.

2. As the pressure is increased from 500 to 1500 p.s.i.:

   a. Sulfur content of the product decreases.
   b. Nitrogen content of the product decreases.
   c. Catalyst deposit decreases and catalyst life increases.
   d. Liquid product recovery increases rapidly between 1000 and 1500 p.s.i.
   e. Naphtha production increases with pressure.
   f. Hydrogen consumption increases with pressure.
   g. Pressure has little effect upon the volume of reaction gases.

3. As the hydrogen rate is increased from 1000 to 4000 standard cubic feet per barrel:

   a. Sulfur reduction increases.
   b. Nitrogen reduction increases.
   c. Catalyst deposit decreases.
   d. Liquid product and naphtha yields increase.
   e. Hydrogen consumption increases.

4. As the space velocity is increased from 0.5 to 1.5 volumes of oil per volume of catalyst per hour, little difference in product yields or quality is detected.

Based on the conclusions listed above, optimum conditions for the hydrogenation of coker distillate to produce Diesel fuels and jet fuels are fairly well established.

These conditions are:

1. Catalyst temperature - 825° to 850° F.

2. Reaction pressure - 1000 to 1500 p.s.i.

3. Hydrogen rate - 2000 to 4000 SCF/bbl.

4. Space velocity - 0.5 to 1.5 Vo/Vc/hr.

A low octane gasoline also is produced under the above conditions. This gasoline is suceptible to catalytic reforming with good yields of specification-grade gasoline.

If gasoline were the primary product desired from hydrogenating of coker distillate, catalyst temperature and space velocity would have to be increased and reaction pressure decreased. Optimum conditions for this operation, although not known exactly, probably lie within the ranges:

1. Catalyst temperature - 950° to 980° F.

2. Reaction pressure 400 to 800 p.s.i.

3. Space velocity - around 5.0 L.H.S.V.

4. Hydrogen rate - around 2000 SCF/bbl.

Separating the light naphtha before hydrogenation results in larger over-all yields of gasoline than can be obtained by hydrogenating the entire coker distillate. The light naphtha, containing large amounts of olefins and relatively low amounts of sulfur and gum, is blended after caustic treatment with the naphtha from the hydrogenated heavy material to give a specification-grade gasoline with higher octane sensitivity.

HYDROGENATION OF WHOLE NAPHTHA

Introduction

Four hydrogenation runs were made over cobalt molybdate catalyst charging the debutanized naphtha from recycle thermal cracking of N-T-U shale oil. The raw naphtha was produced during Rifle cracking run 26, test periods 1 and 2. Because the raw naphtha contained a large amount of C_3 and C_4 hydrocarbons which could not be condensed satisfactorily in the recovery system of the laboratory hydrogenation unit, it was debutanized before it was charged to the hydrogenation unit. Material balances for the hydrogenation runs were based upon the debutanized naphtha charge stock, but it is quite probable that in a commercial unit the whole naphtha, i.e., naphtha containing the C_3 and C_4 fraction, would be charged to the hydrogenation unit and the light ends recovered as part of the product.

Conditions, Material Balances, and Results

Table 13 shows process conditions and material balances for the hydrogenation studies made with the debutanized naphtha. Three runs were made at 400 p.s.i. pressure to investigate the effect of different operating temperatures. One run, Cat. run 178, was made at 200 p.s.i. to obtain information concerning the effect of pressure on hydrogenation. Process

Table 13.--$CoMoO_4$ hydrogenation of whole naphtha from crude shale oil

	Cat. Run #178	Cat. Run #177	Cat. Run #176	Cat. Run #175
Process conditions:				
Ave. temp., °F.	943	961	979	1001
Furnace temp., °F.	875	850	875	900
Pressure, p.s.i.	200	400	400	400
L. H. S.V.	5.0	5.0	5.0	5.0
Vc/Vc	10	10	10	10
H_2 flow, SCF/bbl.	2000	2000	2000	2000
H_2 cons., SCF/bbl.	319	762	775	889
Effluent gas, SCF/bbl.	1906	1478	1554	1634
Cat. depos., wt. percent cat.	4.9	4.0	6.2	7.1
Material balances:				
Gasoline, vol. percent	88.8	89.7	86.7	84.3
Gasoline, wt. percent	86.6	86.0	83.3	81.0
Polymer, vol. percent	2.6	2.6	1.9	2.4
Polymer, wt. percent	2.8	3.1	2.4	3.0
Water, wt. percent	0.8	0.9	0.9	0.9
Coke, wt. percent	0.5	0.5	0.7	0.8
Gas + loss, wt. percent	9.3	9.5	12.7	14.3

conditions and material balances for these runs are presented in table 13, properties of the charge stock and liquid products are shown in table 14, and effluent gas analyses are shown in table 15.

Although the average reaction temperatures for these runs were different, extrapolation of the material balance data indicated that within the pressure range studied the use of higher pressure would result in greater hydrogen consumption, higher liquid recovery, and lower catalyst deposit which should lengthen catalyst life. The higher pressure promoted hydrogenation reactions and, therefore, the products obtained at the higher pressure (with the same reaction temperature) had lower nitrogen content, lower clear octane ratings, and poorer octane sensitivity but had good lead susceptibility. While the gasoline produced at 200 p.s.i. contained little sulfur, that obtained from the 400 p.s.i. runs contained even less.

At the higher temperatures, with constant pressure, liquid recoveries were lower and catalyst deposits higher, but within the temperature range studied hydrogen consumption was little changed. Products produced at the higher temperatures had better clear octane ratings with slightly better sensitivity and somewhat lower lead susceptibility. Temperature had little effect on the sulfur or nitrogen content of the oil.

All gasolines produced from hydrogenating the debutanized naphtha met requirements except for gum and doctor test. Use of better inhibitors and a sweetening process would make specification-grade gasoline from all the gasolines produced with the possible exception of that from run 175.

An over-all material balance for the production of gasoline by thermal cracking of N-T-U crude and hydrogenation of the gasoline is shown in figure 7. Conditions and material balances shown are from run 176. Yields shown are those obtained in the laboratory with the debutanized charge stock. Also shown are the results which might be expected in a commercial operation for which the charge stock was not debutanized. It is probable that in a commercial unit with an efficient recovery system, the light ends would be recovered and would not only improve yields but also would confer additional benefits by raising the octane and volatility of the final product.

Conclusions

Based on the limited amount of data available, several conclusions concerning the effect of operating conditions upon hydrofining whole naphthas are indicated. These conclusions are tentative until substantiated by duplicate runs.

These conclusions are:

Table 14.— $CoMoO_4$ hydrogenation of whole naphtha from crude shale oil

	Charge	Cat. Run #178	Cat. Run #177	Cat. Run #176	Cat. Run #175
Ave. temp., °F.		943	961	979	1001
Pressure, p.s.i.g.		200	400	400	400
Gasoline properties					
Yield, vol. percent charge	----	88.8	89.7	86.7	84.3
Gravity, °A.P.I.	51.9	57.0	58.7	58.5	56.8
ASTM dist., °F.					
IBP	99	110	102	110	110
10	167	161	153	151	143
50	288	268	258	259	243
90	375	369	390	382	358
EP	400	407	395	396	396
Rec., vol. percent	96.5	96.0	95.5	92.0	96.0
Res., vol. percent	1.4	0.5	1.5	1.0	1.0
Loss, vol. percent	2.1	3.5	3.0	7.0	3.0
Sulfur, wt. percent	0.71	0.04	0.02	0.01	0.02
Nitrogen, wt. percent	0.99	0.54	0.38	0.35	0.35
Tar acids, vol. percent	1.0	0.8	2.0	1.8	1.2
Tar bases, vol. percent	7.2	5.8	4.6	4.6	4.8
Paraffins, vol. percent	29	55	64	65	56
Naphthenes, vol. percent	6	8	3	0	2
Olefins, vol. percent	47	11	8	6	7
Aromatics, vol. percent	18	26	25	29	35
Octane, motor, clear	64.7	63.1	62.5	65.4	68.3
+ 1 ml. TEL	69.0	71.0	71.8	75.3	77.4
+ 3 ml. TEL	73.0	78.4	78.5	80.9	82.1
Octane, research, clear	75.4	69.6	67.6	70.0	74.5
+ 1 ml. TEL	77.8	76.9	76.0	78.7	81.9
+ 3 ml. TEL	81.3	84.2	1/ 84.0	1/ 86.4	1/ 88.5
ASTM gum, mg./100 ml.	671	1/ 13.8	1/ 10.6	1/ 8.6	1/ 40.0
Cu. dish gum, mg./100 ml.	1499	1/ 53.8	1/ 25.5	1/ 23.8	1/ 57.4
Induction period, hrs.	0.33	1/ 8	1/ 24+	1/ 24+	1/ 24+
Doctor	Sour	Sour	Sour	Sour	Sour
Polymer properties					
Yield, vol. percent charge		2.6	2.6	1.9	2.4
Gravity, ° A.P.I.		41.2	20.8	16.0	14.1
Sulfur, wt. percent		0.27	0.09	0.11	0.15
Nitrogen, wt. percent		1.32	0.83	0.81	0.61

1/ Inhibited with 0.032 #/bbl. U.O.P. #5.

Table 15.— Gas Analyses, $CoMoO_4$ Hydrogenation of Whole Naphtha from Crude Shale Oil

	Cat. Run #178	Cat. Run #177	Cat. Run #176	Cat. Run #175
Process conditions				
Ave. temp., °F.	943	961	979	1001
Pressure, p.s.i.g.	200	400	400	400
Effluent gas, SCF/bbl.	1906	1478	1554	1634
Gas analyses				
Hydrogen	86.1	85.6	81.9	73.4
Methane	2.4	4.6	6.2	10.2
Ethane	2.0	4.2	4.8	7.5
Propane	1.4	2.6	3.4	4.3
Butanes	1.2	1.5	2.0	1.9
Pentanes	0.6	0.6	0.4	
Ethene				0.1
Propene	0.1			0.5
Butenes	0.2	0.2	0.1	0.4
Pentenes	0.1	0.1	0.1	
Carbon dioxide	0.1			0.2
Carbon monoxide	0.2		0.2	0.1
Nitrogen	5.7	0.6	0.9	1.4
Total	100.0	100.0	100.0	100.0
Ave. molecular weight	6.4	6.4	7.5	9.3

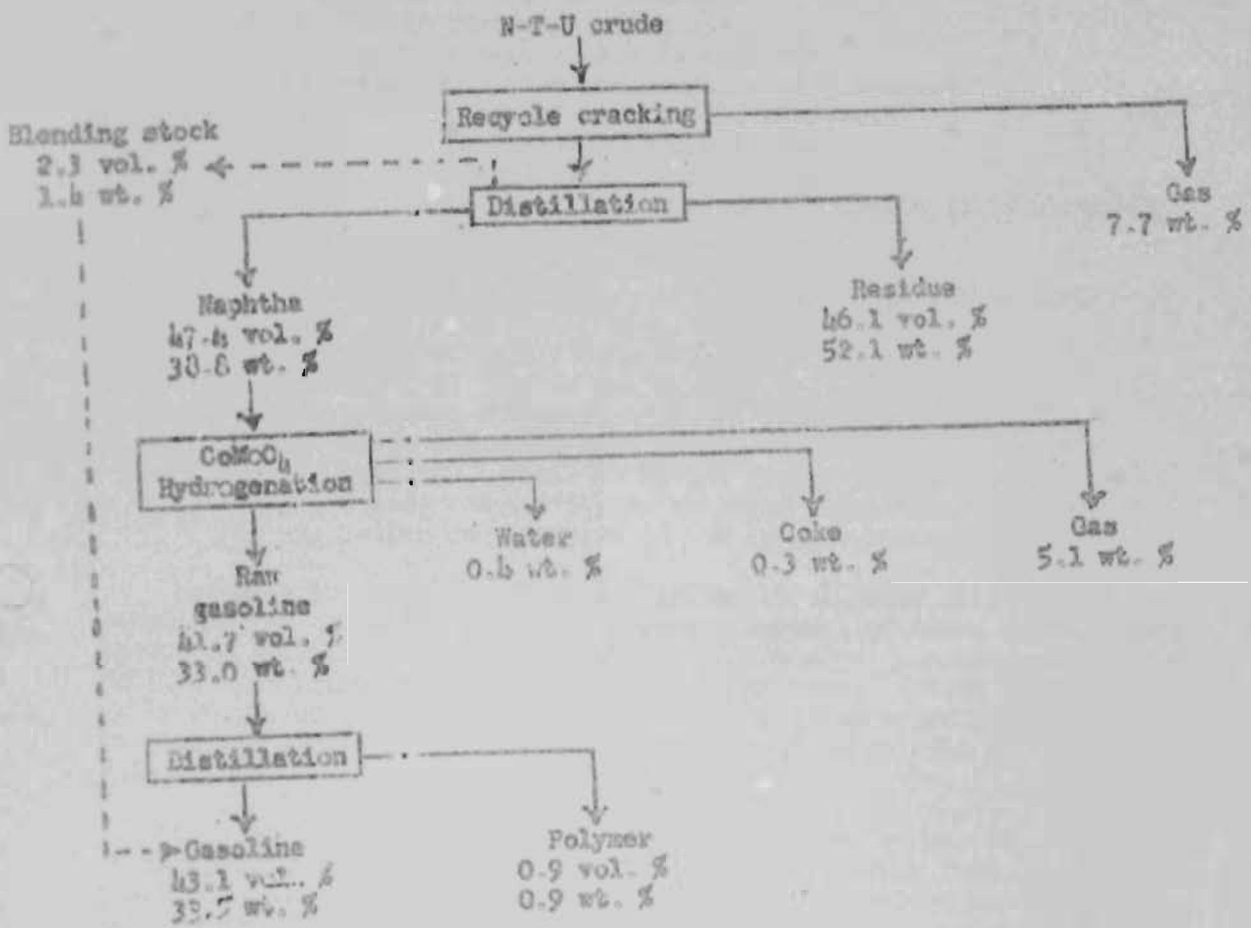

Figure 7.--Material balances, Cat. Run. #176, hydrofining whole naphtha1/

1/ No loss basis.

1. As the pressure is increased:

   a. Catalyst life is increased.
   b. Liquid recovery is increased.
   c. Hydrogen consumption is increased.
   d. Nitrogen content of gasoline is decreased.
   e. Clear octane of gasoline is decreased.
   f. Octane sensitivity is decreased.
   g. Lead susceptibility is increased.
   h. Additional sulfur reduction is not materially achieved between 200 and 400 p.s.i.

2. As reaction temperature is increased from 961° to 1001° F.:

   a. Liquid recovery is reduced.
   b. Catalyst life is decreased.
   c. Hydrogen consumption is not greatly affected.
   d. Clear octane of gasoline is increased.
   e. Lead susceptibility is not appreciably affected.
   f. Octane sensitivity is slightly increased.
   g. Sulfur and nitrogen is not further reduced.

Based on the tabulated data and on the conclusions listed, optimum conditions of temperature and, to a lesser degree, pressure may be tentatively established. These conditions are: catalyst temperature, 960° to 980° F.; and reaction pressure, 400 p.s.i. or more. Octane requirements would be one of the deciding factors in setting the upper pressure limit. No data are available to indicate optimum space velocities or hydrogen rates.

A major factor to be considered for a refining scheme as outlined in figure 7 is the utilization of the residual material from thermal cracking. The utilization of this residue, 46 percent of the charge, either through further refining (undoubtedly expensive) or by sale as residual fuel oils, will have to be taken under consideration. At the present time, this remains a major stumbling block for this type of refining scheme.

HYDROGENATION OF HEAVY NAPHTHA

Introduction

One of the main disadvantages to upgrading shale gasolines by hydrogenation is the loss of olefins and resulting decrease in sensitivity between motor and research octanes. If a fraction of the shale gasoline could be found that contained considerable amounts of olefins and was not objectionable in other respects, then this fraction could be fractionated out and the balance hydrogenated with an improved gasoline as the end product.

Analyses were made of five percent fractions from the distillation of thermally-cracked shale naphthas.[6] The results of these analyses showed that the fractions boiling below 258° F. (40-50 percent of the naphtha) were relatively low in sulfur and gum, had good octane rating, and contained considerable amounts of olefins. These naphthas, after caustic treating to remove hydrogen sulfide and some of the mercaptans, made excellent blending stock.

Several runs were made in order to select the range of optimum processing conditions to be used for hydrogenating the heavy naphtha. In these survey runs the effects of temperature, pressure, hydrogen rate, and space velocity upon yields and product qualities were investigated. Two of the survey runs gave such remarkable results that the data were worked up in considerable detail to show over-all yields and liquid product properties.

A long run to determine catalyst life was made under conditions selected as being within the optimum ranges determined by these survey runs. The gasoline produced during the initial stages of this run met all requirements for regular grade gasoline without the use of inhibitors.

The data from one of the survey runs made within optimum operating ranges were used in order to calculate the heat of hydrogenation of heavy naphtha.

Effect of Temperature

Three typical runs were selected to show the effect of reaction temperature upon product quality and yield when hydrogenating heavy naphtha. The process conditions and material balances for these runs are given in table 16. The temperatures used were appreciably higher than those used for hydrogenation of coker distillate because higher-octane products were desired.

As the reaction temperature was increased, the amount of gas and coke produced increased while liquid recovery dropped, the decrease being particularly rapid at temperatures over 980° F. The temperature

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6/ O'Keefe, J. A., Brown, J. F., Shale-Oil Refining Research, Pet. 423-17, U. S. Bur. of Mines, Laramie Station Project Reports, June 1950, July 1950, and November 1950.

Table 16.—Temperature survey, $CoMoO_4$ hydrogenation of heavy naphtha.

	Cat run 198	Cat run 187	Cat run 186
Process conditions:			
Length of run, hrs.	3	2.5	3
Temperature, °F.	947	984	1011
Pressure, p.s.i.	600	600	600
L.H.S.V.	5.0	5.0	5.0
Vo/Vc	15.0	12.5	15.0
Hydrogen flow, scf./bbl.	2000	2000	2000
Hydrogen consumed, scf./bbl.	910	1054	1031
Effluent gas, scf./bbl.	1425	1590	1665
Cat. deposit, wt. % cat.	5.2	8.0	12.1
Material balances:			
Liquid product, vol.%	92.2	87.2	79.9
" " , wt.%	86.9	82.9	76.1
Gasoline, vol. %	86.1	84.1	77.3
" , wt. %	80.0	79.4	73.1
Polymer, vol. %	6.1	2.9	2.5
" , wt. %	6.9	3.5	3.0
Water, wt. %	1.5	1.2	1.3
Coke, wt. %	0.3	0.7	0.8
Gas + loss, wt. %	11.3	15.2	21.8

had little effect upon hydrogen consumption, however. Although the figures showed an increased consumption at the higher temperatures, the accuracy of this determination was such that a small change in hydrogen consumption had little meaning.

Liquid product analyses for this series of runs are given in table 17. The data show that as the reaction temperature was increased, sulfur removal was slightly greater, but nitrogen removal was less. Unleaded octane numbers were increased with temperature as was the sensitivity between motor and research octane numbers, but lead susceptibility was decreased even though sulfur content was decreased. Due to the wide difference between gum contents of the various charge stocks it was difficult to correlate the effect of temperature upon gum. Apparently, the gum passed through a minimum when treating around 980° F.

The gas analyses for this series of runs are given in table 18. It is quite apparent that as the temperature was increased, the volume of cracking gases, such as methane, was increased. The increase was relatively uniform for methane over the temperature range studied.

The best processing temperatures lie between 950° and 980° F. At temperatures below 950° F. octane ratings are apt to be too low. At temperatures above 980° F. octane numbers will be high but yields will be lower. Gum contents may be high when processing above 980° F.

Effect of Pressure

Data in typical runs showing the effect of pressure on hydrogenation of heavy naphtha are given in table 19. The pressure range covered in this series was 200 to 800 p.s.i., higher pressures not being used because of the deleterious effect of pressure upon octane number.

As reaction pressure was increased, there was a uniform decrease in catalyst deposit which indicated longer catalyst activity at the higher pressure. Hydrogen consumption increased with pressure, the increase being particularly rapid between 200 and 400 p.s.i. The volume of liquid product was essentially constant over the pressure range studied as was the volume of reformed gasoline produced.

The liquid product analyses, table 20, and the effluent gas analyses, table 21, indicate additional advantages in using higher pressure. The sulfur and nitrogen content were lower at the higher pressures. Both copper dish gum and A.S.T.M. gum decreased as the pressure was increased. Care must be used when comparing octane ratings at the various pressures because of differences in charge stocks used throughout this series.

Table 17.—Liquid product inspections, temperature survey, $CoMoO_4$ hydrogenation of heavy naphtha.

Run no.	Charge	198	Charge	187	186
Charge, sample no. RRS-	51-537	51-537	51-469	51-469	51-469
Temperature, °F.		947		984	1011
Whole product:					
Gravity, °API		49.1		47.5	47.3
Gasoline:					
Gravity, °API	38.7	48.1	38.8	47.9	47.1
A.S.T.M. Dist., °F at 760					
IBP	298	131	265	115	110
10	312	221	315	187	158
50	341	312	340	303	297
90	390	367	391	376	369
EP	418	400	417	435	416
Rec., vol. %	97.5	99.0	97.0	96.0	96.0
Res., " "	2.0	0.5	2.2	1.0	1.0
Loss, " "	0.5	0.5	0.8	3.0	3.0
Sulfur, wt. %	1.01	0.10	1.06	0.02	0.02
Nitrogen, wt. %	1.42	0.55	1.64	0.60	0.76
Paraffins, vol. %	21	55	31	52	45
Naphthenes, " "	3	2	4	0	0
Olefins, " "	49	8	37	6	6
Aromatics, " "	27	35	28	42	49
Tar acids, " "	1.7	0.7	1.8	1.3	1.0
Tar bases, " "	14.3	5.2	8.7	6.2	7.7
Octane, motor, clear	64.8	60.2	66.0	67.6	72.8
" " +1 ml. TEL	67.1	69.0	69.8	76.0	79.3
" " +3 ml. TEL	69.5	76.9	72.3	81.2	82.4
" research, clear	74.7	68.0	73.4	75.3	82.0
" " +1 ml. TEL	75.3	75.5	75.9	81.8	87.4
" " +3 ml. TEL	78.0	84.0	79.3	87.8	91.8
A.S.T.M. Gum, mg./100 ml.	2026	10.8	1656	5.2	6.8
Cu dish gum " " "	3002	26.6	5034	31.9	55.0
Induction period, hrs.	0.25	+24	0.25	+24	+24
Doctor	sour	sweet	sour	sweet	sweet
Corrosion	neg.	neg.	pos.		
R.V.P. p.s.i.a. at 100° F.		4.0			

Table 18.--Gas analyses, temperature survey, $CoMoO_4$ hydrogenation of heavy naphtha.

	Cat. run 198	Cat. run 187	Cat. run 186
Process conditions:			
Temp. °F.	947	984	1011
Pressure, p.s.i.	600	600	600
L. H. S. V.	5.0	5.0	5.0
Vo/Vc	15.0	12.5	15.0
Hydrogen flow, scf./bbl.	2000	2000	2000
" consumed, scf./bbl.	910	1054	1031
Effluent gas, scf./bbl.	1425	1580	1665
Cat. deposit, wt.% cat.	5.2	8.0	12.1
Gas analyses:			
Hydrogen	79.7	73.8	62.5
Methane	7.9	11.2	15.4
Ethane	5.6	7.6	11.2
Propane	4.3	4.9	7.4
Butanes	1.7	1.6	2.6
Pentanes	0.2	0.4	0.5
Ethylene	0.3		
Propylene	Tr.		0.1
Butenes	0.1	0.2	0.2
Pentenes			0.1
Carbon dioxide	0.1		
Carbon monoxide		0.3	
Total	99.9	100.0	100.0
Avg. molecular wt.	7.7	9.1	12.4

Table 19.--Pressure survey, $CoMoO_4$ hydrogenation of heavy naphtha.

	Cat. run #183	Cat. run #180	Cat. run #198	Cat. run #208
Process conditions:				
Length of run, hrs.	3.0	3.0	3.0	3.0
Temperature, °F.	960	961	947	942
Pressure, p.s.i.	200	400	600	800
L.H.S.V.	5.0	5.0	5.0	5.0
Vo/Vc	15.0	15.0	15.0	15.0
Hydrogen flow, scf./bbl.	2000	2000	2000	2000
Hydrogen consumed, scf./bbl.	87	721	910	--
Effluent gas, scf./bbl.	2610	1650	1425	1460
Cat. deposit, wt. % cat.	10.0	7.7	5.2	4.6
Material balances:				
Liquid product, vol. %	92.3	93.1	92.2	93.3
" " , wt. %	89.8	89.4	86.9	87.1
Gasoline, vol. %	88.1	87.6	86.1	90.7
" wt. %	85.1	83.4	80.0	84.7
Polymer, vol. %	4.2	5.5	6.1	2.6
" wt. %	4.7	6.0	6.9	2.4
Water, wt. %	0.9	0.9	1.5	1.5
Coke, wt. %	0.7	0.5	0.3	0.3
Gas + loss, wt. %	8.6	9.2	11.3	11.1

Table 20.--Liquid product inspections, pressure survey, $CoMoO_4$ hydrogenation of heavy naphtha.

Run no.	Charge	183	180	Charge	198	Charge	208
Charge, sample #RRS-	51-469	51-469	51-469	51-537	52-537	51-764	51-764
Pressure, p.s.i.		200	400		600		800
Whole product:							
Gravity, °API		43.6	45.8		49.1		50.3
Gasoline:							
Gravity, °API	38.8	43.9	46.8	38.7	48.1	38.3	50.2
A.S.T.M. dist., °F. at 760							
IBP	265	138	117	298	131	279	106
10	315	258	229	312	221	315	184
50	340	322	308	341	312	343	307
90	391	374	364	390	367	389	369
EP	417	399	407	418	400	415	398
Rec., vol.%	97.0	97.5	97.0	97.5	99.0	97.0	96.5
Res., " "	2.2	0.5	0.5	2.0	0.5	2.5	0.6
Loss, " "	0.8	2.0	2.5	0.5	0.5	0.5	2.9
Sulfur, weight %	1.06	0.16	0.02	1.01	0.10	0.97	nil
Nitrogen " "	1.64	1.16	0.86	1.42	0.55	1.71	0.43
Paraffins, vol. %	31	42	52	21	55	30	62
Naphthenes, " "	4	8	5	3	2	5	0
Olefins, " "	37	14	5	49	8	34	3
Aromatics, " "	28	36	38	27	35	31	35
Tar acids, " "	1.8	0.2	0.8	1.7	0.7	1.8	1.0
Tar bases, " "	8.7	9.2	7.4	14.3	5.2	10.0	4.0
Octane, motor, clear	66.0	68.1	63.8	64.8	60.2	69.4	62.1
" " ,+1 ml.TEL	69.8	73.1	72.7	67.1	69.0	71.2	70.0
" " ,+3 ml.TEL	72.3	77.2	79.0	69.5	76.9	73.8	76.0
" ,research, clear	73.4	75.7	70.7	74.7	68.0	74.6	68.5
" " ,+1 ml.TEL	75.9	79.9	76.5	75.3	75.5	76.6	75.6
" " ,+3 ml.TEL	79.3	84.6	84.1	78.0	84.0	79.0	83.1
A.S.T.M. gum, mg./100 ml.	1656	17.8	8.8	2026	10.8	2026	2.8
Cu dish gum, " " "	5034	47.7	39.1	3002	26.6	3006	17.9
Induction period, hrs.	0.25	0.25	+24	0.25	+24	0.25	+24
Doctor	Sour	Sweet	Sweet	Sour	Sweet	Sour	Sweet
Corrosion	Pos.			Neg.	Neg.	Pos.	Neg.
R.V.P., p.s.i.a. at 100°F.					4.0		5.5

Table 21.—Gas analyses, pressure survey, $CoMoO_4$ hydrogenation of heavy naphtha.

	Cat. run #183	Cat. run #180	Cat. run #198	Cat. run #208
Process conditions:				
Temp. °F.	960	961	947	942
Pressure, p.s.i.	200	400	600	800
L.H.S.V.	5.0	5.0	5.0	5.0
Vo/Vc	15.0	15.0	15.0	15.0
Hydrogen flow, scf./bbl.	2000	2000	2000	2000
" consumed, scf./bbl.	87	721	910	--
Effluent gas, scf./bbl.	2610	1650	1425	1460
Cat. deposit, wt. % cat.	10.0	7.7	5.2	4.6
Gas analyses:				
Hydrogen	89.6	84.6	79.7	No gas analysis
Methane	4.2	6.7	7.9	
Ethane	3.1	4.9	5.6	
Propane	1.6	2.6	4.3	
Butanes	0.6	0.8	1.7	
Pentanes			0.2	
Ethylene	0.1		0.3	
Propylene	0.3	0.1	Tr.	
Butenes	0.2	0.1	0.1	
Pentenes				
Carbon dioxide			0.1	
Carbon monoxide	0.3	0.2		
Total	100.0	100.0	99.9	
Avg. molecular wt.	6.0	6.0	7.7	

From a comparison of the octane number of the hydrogenated gasoline with the octane number of the charge for each run, it was evident that pressure had a deleterious effect on clear octane number both motor and research. Lead response, however, was higher at the more elevated pressures with the end result being that an improved octane number gasoline was produced, even at 800 p.s.i. A slight decrease in sensitivity was noticed as the pressure was increased.

Gas analyses from these runs indicate that reaction gases from the runs at lower pressure were richer in hydrogen due to the low hydrogen consumption at the lower pressure. The actual volume of methane and ethane produced did not vary between 200 and 600 p.s.i. although slightly more of the heavier gases (propane, butane) were produced at the higher pressures.

The pressure effects discussed above indicate that product quality is best when hydrogenating between 600 and 800 p.s.i. At pressures below 600 p.s.i., gum content of the hydrogenated gasoline will be high and catalyst life will be shortened. Above 800 p.s.i., octane numbers will be low.

Effect of Hydrogen Rate

Four typical runs showing the effect of a third operating variable, hydrogen rate, are listed in table 22. The hydrogen rate was varied between 1,000 and 4,000 standard cubic feet per barrel. (As used throughout this work, standard cubic feet are defined as cubic feet at one atmosphere and 70° F.) Unfortunately, due to the difficulty of obtaining good temperature control, a temperature variation of 40° F. occurred in this series of runs. Many of the observations, therefore, have to be qualified to include temperature deviations.

The effect of hydrogen rate upon catalyst deposit and catalyst life was quite apparent. At 4,000 cubic feet of hydrogen, taking under consideration temperature effects, the catalyst deposit was less than 20 percent of that at 1,000 cubic feet. This meant that increasing the hydrogen rate from 1,000 to 4,000 cubic feet per barrel gave a large increase in catalyst life.

No hydrogen consumption figure was available for the run made at 4,000 cubic feet, but the balance of the data indicated that hydrogen consumption was increasing with hydrogen rate, with the major increase appearing between 1,000 and 2,000 cubic feet per barrel. The effect of hydrogen flow rate on liquid recovery is indeterminate from the data shown in table 22 because of temperature deviations. However, other work in the past showed that a slight increase in liquid recovery was possible when the hydrogen rate was raised.

Table 22.—Hydrogen rate survey, $CoMoO_4$ hydrogenation of heavy naphtha.

	Cat. run #196	Cat. run #187	Cat. run #189	Cat. run #195
Process conditions:				
Length of run, hrs.	3.0	2.5	3.0	3.0
Temperature, °F.	961	984	983	1008
Pressure, p.s.i.	600	600	600	600
L.H.S.V.	5.0	5.0	5.0	5.0
Vo/Vc	15.0	12.5	15.0	15.0
Hydrogen flow, scf./bbl.	1000	2000	3000	4000
Hydrogen consumed, scf./bbl.	336	1054	1136	
Effluent gas, scf./bbl.	780	1580	2410	5310
Cat. deposit, wt.% cat.	16.2	8.0	4.8	2.9
Material balances:				
Liquid product, vol. %	90.1	87.2	89.7	85.0
" " , wt. %	86.4	82.9	84.8	80.0
Gasoline, vol. %	84.2	84.1	85.0	82.9
" , wt. %	79.7	79.4	79.5	77.6
Polymer, vol. %	5.9	2.9	4.7	2.1
" , wt. %	6.7	3.5	5.3	2.4
Water, wt. %	0.9	1.2	1.3	1.2
Coke, wt. %	1.1	0.7	0.3	0.2
Gas + loss, wt. %	11.6	15.2	13.6	18.6

Liquid product analyses for these runs, shown in table 23, point out many advantages for high hydrogen flow rates. The sulfur content of the gasoline was reduced sharply between 1,000 and 2,000 cubic feet of hydrogen, with little further reduction at higher rates. Nitrogen content on the other hand decreased continuously over the entire range. The gum content of the refined gasoline apparently passed through a minimum between 2,000 and 3,000 cubic feet per barrel although differences in charge stocks and reaction temperature may account for part of this phenomenon. Actually the high reaction temperature used for the 4,000 cubic foot run had a deleterious effect upon gum. It is quite probable, therefore, that under identical temperature conditions, the gum content would decrease throughout the hydrogen rate range studied.

Increasing the hydrogen rate did not affect greatly clear octane ratings although a slight decrease was detected. Sensitivity of the fuel was only slightly affected, but lead susceptibilities were better at the higher hydrogen rates.

Gas analyses for this series of runs are listed in table 24.

Optimum conditions for hydrogenation, therefore, would include hydrogen rates between 2,000 and 3,000 standard cubic feet per barrel. Below 2,000 cubic feet, sulfur reduction is lessened, catalyst life is shortenened, and gum contents high. Above 3,000 cubic feet of hydrogen, additional equipment and gas handling costs entailed probably are not warranted by the small advantage gained in product quality.

Effect of Space Velocity

The fourth processing variable, space velocity, was studied in considerable detail for its effect upon hydrogenation of heavy naphthas. Space velocities ranging from 2.5 to 10.0 volumes of oil per volume of catalyst per hour were studied. Conditions and material balances for some of these runs are shown in table 25. It is apparent that space velocities within the range studied had little effect upon hydrogen consumption. Catalyst deposit, however, was lowest at a space velocity of 7.5, increasing rapidly between 7.5 and 10. Liquid recovery and gasoline production were quite low at a space velocity of 2.5, but were essentially constant and much higher between 5.0 and 10.0.

Although the volume of gas produced remained essentially constant over the range studied, the weight of gas produced was considerably higher at a low space velocity. The gas analyses in table 27 show that a much heavier gas was formed at a space velocity of 2.5 than at higher space velocities. This indicates that a greater depth of cracking occurred at the lower space velocity.

The analytical data for the liquid product from these runs are shown in table 26. These data show that space velocities above 7.5

Table 23.--Liquid product analyses, hydrogen rate survey, $CoMoO_4$ hydrogenation of heavy naphtha.

Run no.	charge	charge	196	187	189	195
Charge, sample #RRS-	51-537	51-469	51-537	51-469	51-537	51-537
Hydrogen rate, scf./bbl.			1000	2000	3000	4000
Whole product:						
Gravity, °API			46.2	47.5	48.4	49.6
Gasoline:						
Gravity, °API	38.7	38.8	45.9	47.9	49.0	48.9
ASTM dist. °F. at 760						
IBP	298	265	125	115	124	132
10	312	315	218	187	203	198
50	341	360	314	303	298	298
90	390	391	370	376	357	363
EP	418	417	399	435	384	396
Rec., vol. %	97.5	97.0	98.7	96.0	97.5	97.8
Res., " "	2.0	2.2	0.5	1.0	0.6	0.6
Loss, " "	0.5	0.8	0.8	3.0	1.9	1.5
Sulfur, wt. %	1.01	1.06	0.12	0.02	0.02	0.03
Nitrogen, wt. %	1.42	1.64	0.82	0.60	0.40	0.32
Paraffins, vol. %	21	31	44	52	55	47
Naphthenes, " "	3	4	6	0	1	6
Olefins, " "	49	37	8	6	9	6
Aromatics, " "	27	28	42	42	35	41
Tar acids, " "	1.7	1.8	0.4	1.3	0.4	1.6
Tar bases, " "	14.3	8.7	2.8	6.2	4.3	1.6
Octane, motor, clear	64.8	66.0	66.0	67.6	63.0	63.4
" " +1 ml. TEL	67.1	69.8	72.6	76.0	70.4	72.0
" " +3 ml. TEL	69.5	72.3	79.2	81.2	78.9	79.0
" research, clear	74.7	73.4	74.4	75.3	70.5	71.9
" " +1 ml. TEL	75.3	75.9	81.1	81.8	78.4	79.9
" " +3 ml. TEL	78.0	79.3	86.3	87.8	85.0	87.2
A.S.T.M. gum, mg./100 ml.	2026	1656	17.0	5.2	9.0	7.2
Cu dish gum, " " "	3002	5034	128.7	31.9	17.2	34.4
Induction period, hrs.	0.25	0.25	+24	+24	+24	5
Doctor	Sour	Sour	sl.sour	sweet	sweet	sweet
Corrosion	neg.	pos.	neg.		pos.	neg.
R.V.P., p.s.i.a. at 100° F.			4.3		4.9	3.0

Table 24.—Gas analyses, hydrogen rate survey, $CoMoO_4$ hydrogenation of heavy naphtha.

	Cat. run #196	Cat. run #187	Cat. run #189	Cat. run #195
Process conditions:				
Temperature, °F.	961	984	983	1008
Pressure, p.s.i.	600	600	600	600
L.H.S.V.	5.0	5.0	5.0	5.0
Vo/Vc	15.0	12.5	15.0	15.0
Hydrogen flow, scf./bbl.	1000	2000	3000	4000
Hydrogen consumed, scf./bbl.	336	1054	1136	-664(?)
Effluent gas, scf./bbl.	780	1580	2410	5310
Cat. deposit, wt. % cat.	16.2	8.0	4.8	2.9
Gas analyses:				
Hydrogen	88.5	73.8	79.1	88.1
Methane	4.3	11.2	7.7	4.1
Ethane	3.2	7.6	5.8	3.1
Propane	2.3	4.9	4.2	2.5
Butanes	0.9	1.6	1.6	1.2
Pentanes		0.4	0.8	0.5
Ethylene	0.2		0.1	0.1
Propylene	0.1			
Butenes	0.3	0.2	0.3	0.2
Pentenes			0.2	0.1
Carbon dioxide	0.1		0.1	0.1
Carbon monoxide	Tr.	0.3		
Total	99.9	100.0	99.9	100.0
Avg. molecular wt.	5.3	9.1	8.3	5.8

Table 25.—Space velocity survey, $CoMoO_4$ hydrogenation of heavy naphtha

	Cat. Run #184	Cat. Run #181	Cat. Run #199	Cat. Run #185
Process conditions:				
Length of run, hrs.	3	3	2	3
Temperature, °F.	976	977	972	982
Pressure, p.s.i.	400	400	400	400
L.H.S.V.	2.5	5.0	7.5	10.0
Vo/Vc	7.5	15.0	15.0	30.0
Hydrogen flow, scf./bbl.	2000	2000	2000	2000
Hydrogen consumed, scf./bbl.	945	716	582	653
Effluent gas, scf./bbl.	1730	1700	1810	1760
Cat. deposit, wt. % cat.	10.8	9.3	6.8	11.3
Material balances:				
Liquid product, vol. %	81.1	90.8	90.8	91.8
Liquid product, wt. %	77.3	87.5	87.4	88.6
Gasoline, vol. %	78.3	88.4	87.9	88.0
Gasoline, wt. %	73.9	84.2	84.0	84.3
Polymer, vol. %	2.7	2.9	2.9	3.6
Polymer, wt. %	3.4	3.3	3.3	4.3
Water, wt. %	1.5	0.9	1.0	0.7
Coke, wt. %	1.4	0.6	0.5	0.4
Gas + loss, wt. %	19.8	11.0	11.2	10.3

Table 26.--Liquid product analyses, space velocity survey, $CoMoO_4$ hydrogenation of heavy naphtha.

Run no. Charge, sample #RRS- L.H.S.V.	Charge 51-469	Charge 51-679	184 51-469 2.5	181 51-469 5.0	199 51-679 7.5	185 51-469 10.0
Whole product:						
Gravity, °API			47.1	54.3	45.7	45.0
Gasoline:						
Gravity, °API	38.8	39.1	47.7	46.6	45.7	44.4
A.S.T.M. dist. °F at 760						
IBP	265	285	111	113	147	131
10	315	310	174	206	250	228
50	340	341	297	310	320	318
90	391	-	372	371	371	372
E.P.	417	430	405	401	403	399
Rec., vol. %	97.0	98.2	95.5	97.5	98.9	98.0
Res., vol. %	2.2	1.3	0.5	0.5	0.4	0.5
Loss, " "	0.8	0.5	4.0	2.0	0.7	1.5
Sulfur, wt. %	1.06	0.98	0.09	nil	0.09	0.22
Nitrogen, " "	1.64	1.40	0.74	0.88	0.74	1.25
Paraffins, vol. %	31	34	47	50	52	42
Naphthenes, " "	4	4	0	5	3	3
Olefins, " "	37	35	5	8	9	18
Aromatics, " "	28	27	48	37	36	36
Tar acids, " "	1.8	2.8	0.7	0.6	0.4	0.2
Tar bases, " "	8.7	6.9	6.3	7.7	7.3	9.2
Octane, motor, clear	66.0	62.8	72.9	67.2	63.6	68.9
" " +1 ml.TEL	69.8	64.9	77.9	74.5	71.5	73.4
" " +3 ml.TEL	72.3	68.6	81.6	80.4	76.8	77.1
" research, clear	73.4	70.8	82.1	73.1	70.8	77.3
" " +1 ml.TEL	75.9	72.4	88.6	79.6	77.4	82.6
" " +3 ml.TEL	79.3	76.3	92.6	85.6	84.6	87.1
A.S.T.M. gum, mg./100 ml.	1656		26.8	20.0	7.8	89.4
Cu dish gum, " " "	5034		54.5	47.5	51.9	280.0
Induction period, hrs.	0.25		+24	+24	+8	+24
Doctor	Sour	Sour	Sweet	Sweet		Sweet
Corrosion	Pos.					
R.V.P., p.s.i.a. at 100° F.						

Table 27.--Gas analyses, space velocity survey, $CoMoO_4$ hydrogenation of heavy naphtha

	Cat. run #184	Cat. run #181	Cat. run #199	Cat. run #185
Process conditions:				
Temp., °F.	976	977	972	982
Pressure, p.s.i.	400	400	400	400
L.H.S.V.	2.5	5.0	7.5	10.0
Vo/Vc	7.5	15.0	15.0	30.0
Hydrogen flow, scf./bbl.	2000	2000	2000	2000
" consumed, scf./bbl.	945	716	582	653
Effluent gas, scf./bbl.	1730	1700	1810	1760
Cat. deposit, wt. % cat.	10.8	9.3	6.8	11.3
Gas analyses:				
Hydrogen	66.6	80.7	84.9	84.7
Methane	14.1	8.1	5.3	6.3
Ethane	10.0	6.1	4.3	4.5
Propane	6.7	3.5	3.0	2.4
Butanes	2.1	1.2	1.4	0.8
Pentanes	0.3			0.1
Ethylene			0.2	0.3
Propylene	0.1	0.1		0.4
Butenes	0.1	0.2	0.2	0.3
Pentenes				0.1
Carbon dioxide			0.1	
Carbon monoxide		0.3	0.2	0.2
Benzene			0.1	
Toluene			0.1	
Total	100.0	100.2	99.8	100.1
Avg. molecular wt.	11.0	7.0	6.4	6.2

were extremely detrimental to product quality. Apparently, a space velocity of 10 permitted a considerable portion of the charge to pass through the unit without being hydrogenated. The sulfur content of the reformed gasoline passed through a minimum at a space velocity of 5.0 while the nitrogen content was essentially uniform at space velocities from 2.5 to 7.5 but increased rapidly thereafter. Gum contents were lowest at space velocities of 5.0 and 7.5.

A comparison of the octanes of the hydrogenated gasolines with the octane ratings of the charge stocks for each run showed that minimum unleaded octane numbers were obtained at space velocities of 5.0 and 7.5. Lead susceptibility, however, was better at these same space velocities. Sensitivity between motor and research octane numbers was not changed essentially by altering the space velocity. In every run in this series, the octane ratings of the products were as good or better than the octane numbers of the charge.

The over-all effect was to give a better product at space velocities between 5.0 and 7.5. Space velocities below 5.0 allowed too great a depth of cracking with its attendant disadvantages, while space velocities over 7.5 did not permit sufficient contact time for necessary hydrogenation reactions to take place.

Light Naphthas and Blending

An important factor in the production of gasoline by naphtha splitting and hydrogenation of the heavy fraction, is the quality of the light naptha blending stock. As mentioned previously, the light naphtha should contain large amounts of olefins for motor sensitivity to compensate for the low olefin content of the hydrogenated heavy gasoline. Other properties of the light naphtha should be such that when blended in proportions that will completely use the stock, the blended gasoline will meet required specifications. Some of the more important properties of a light naphtha suitable for blending in this process are: sulfur, below 0.30 percent; A.S.T.M. gum, below five mg. per 100 ml.; motor octane number, over 75 with less than three ml. of lead; research octane number, five to ten numbers higher than motor octane number; and it should be doctor sweet.

Properties of some of the light naphthas used are shown in table 28. For convenience, properties of the whole naphtha before splitting are included. The first light naphtha produced (RRS-51-468) had most of the desirable properties. It did contain considerable amounts of dissolved hydrogen sulfide, however. Water washing this naphtha, although it removed considerable amounts of hydrogen sulfide, was not sufficient to render the nauhtha doctor sweet. Chemical treating was found to be necessary before the naphtha would meet blending requirements. Five

Table 28.--Properties of light naphthas obtained from thermally cracked shale naphthas by distillation followed by chemical treating.

Type naphtha	Whole	Light	Light	Light	Light
Sample no., RRS-	51-150	51-468	51-509	51-511	51-571
Source, sample no., RRS-		51-150	51-468	51-468	51-150
Chemical treatment	None	None	10% NaOH	Unisol	10% NaOH
Whole naphtha, vol. percent	100	41.4	40.9	40.5	39.4
Gravity, °API	54.0	68.4	68.1	68.3	68.4
A.S.T.M. dist., °F at 760					
IBP	99	96			114
10% recovered	158	135			142
50% "	289	186			187
90% "	384	233			234
E.P.	395	261			246
Rec., vol. %	93.0	96.5			97.5
Res., vol. %	1.1	0.8			0.8
Loss, vol. %	5.9	2.7			1.7
Sulfur, wt. %	0.68	0.26	0.19	0.19	0.22
Nitrogen, wt. %	0.98	0.17			0.05
Tar acids, vol. %	2.0	0.6			1.9
Tar bases, vol. %	10.2	2.2			2.7
Paraffins, vol. %	29	34			34
Naphthenes, vol. %	3	8			9
Olefins, vol. %	50	52			50
Aromatics, vol. %	18	6			7
Octane, motor, clear	66.8	70.0			68.7
Octane, motor, +1 ml. T.E.L.	70.1	73.6			74.6
Octane, motor, +3 ml. T.E.L.	72.8	76.8			79.3
Octane, research, clear	74.4	79.2			79.0
Octane, research, +1 ml. T.E.L.	78.1	83.8			84.8
Octane, research, +3 ml. T.E.L.	81.8	88.2			88.9
A.S.T.M. gum, mg./100 ml.	45	3			1.4
Cu dish gum, mg./100 ml.	643	10			9.5
Induction period, min.	15	485			1440
Doctor	Sour	Sour	Sl.Sour	Sweet	Sweet
Corrosion		Pos.	Neg.	Neg.	Neg.
Inhibitor, lbs. U.O.P. no.5/bbl.	None	0.032			0.032

batch extractions each consisting of washing with 20 percent by volume of 10 percent caustic were required for sweetening, or sweetening could be accomplished by the use of "Unisol" treatment.[7] The data in table 28 show that considerable amounts of sulfur were removed by either process. Another light naphtha was prepared and sweetened by caustic treating. This naphtha when inhibited met all requirements for a satisfactory blending stock.

Inhibiting was necessary to control gum formation as these light naphthas, like other shale-oil fractions, were prone to form gum on standing. The addition of 0.032 pounds per barrel of U.O.P. number 5 inhibitor was sufficient to control gum if the inhibiting was done before the naphtha was exposed to air or sunlight.

Gasoline Production

Figure 8 shows the over-all refining scheme for the production of gasoline by naphtha splitting and hydrogenation of the heavy material. Operating conditions are shown in table 29. The material balances shown for naphtha splitting and hydrogenation are those obtained by use of bench-scale laboratory equipment. The blending stock, indicated by the dotted line in figure 8 represents that portion of the light naphtha that was not condensed in the laboratory distillation unit. This light material should be added to the finished gasoline for two reasons. First, a continuous, pressurized still would retain a considerable portion of the C_3 and C_4 fraction; and second, gasolines from the laboratory hydrogenation unit invariably had a low vapor pressure. The addition of the light material to the blended gasoline, the properties of which are shown in table 30, would change slightly the indicated values. Improvement would be detected in octane and volatility.

The gasoline produced by blending met requirements for regular-grade gasoline except for gum content. The gum that appeared in the blended gasoline was higher than the gum in either of the component gasolines. As the light naphtha was properly inhibited, this gum undoubtedly formed in the heavy gasoline portion. Hydrogenating at the elevated temperature did not completely remove the gum-forming constituents and gum would form unless the gasoline was properly inhibited.

The data show the influence of the light naphtha in improving the sensitivity of the blend. Clear octane improvement was also achieved by the addition of light naphtha. Lead susceptibility was decreased, although less lead was required for the blend to reach research octane number specifications than was required for the heavy gasoline alone.

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[7] Mason, Bent, McCullough, Proc. A.P.I., 22 (III), 45 (1941).

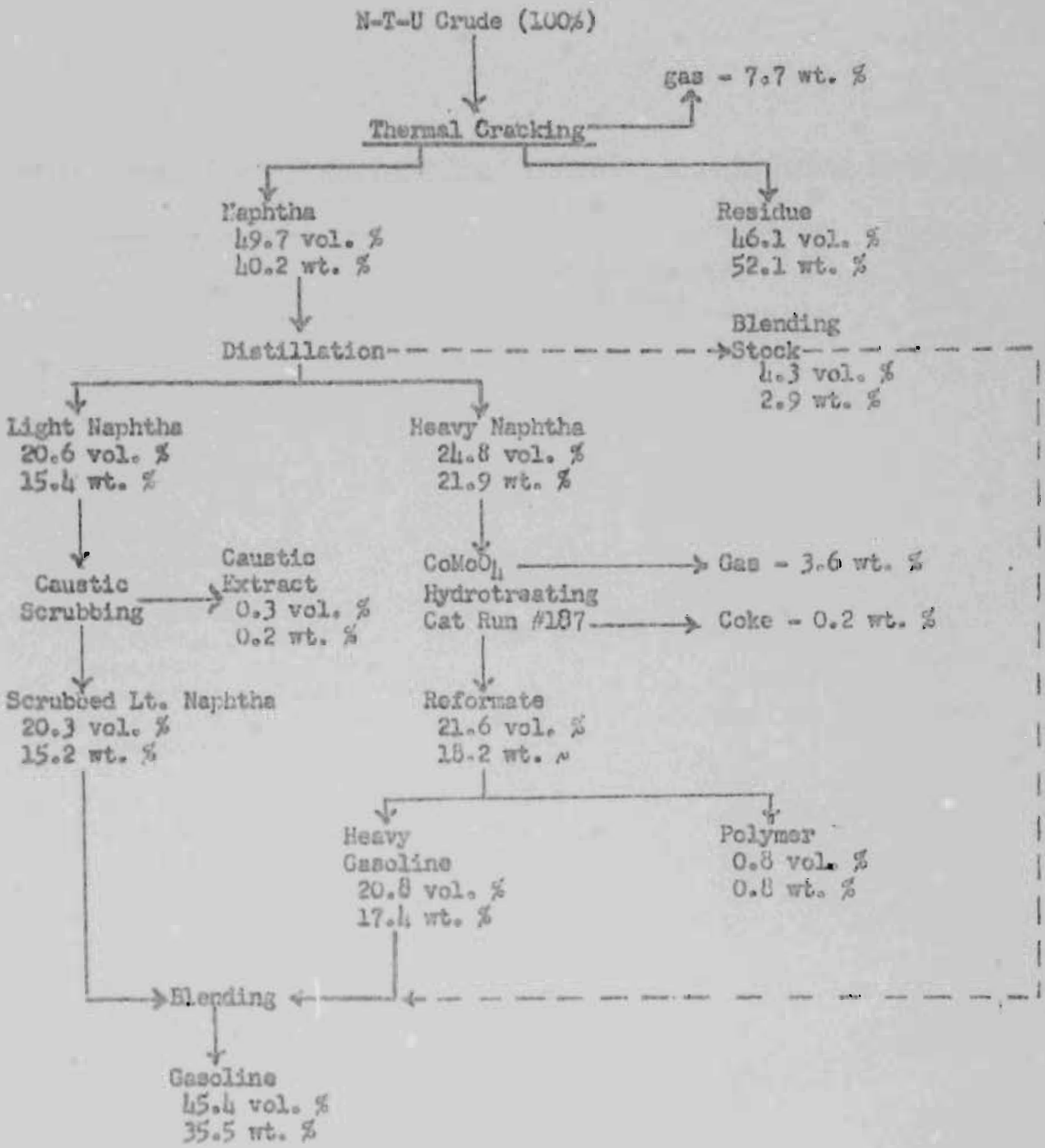

Figure 8.--Material Balances, Gasoline Production by Hydrofining Heavy Naphtha[1]

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[1] No loss basis

Table 29.—Process conditions, gasoline production by hydrofining heavy naphtha

Process	Recycle Thermal Cracking		$CoMoO_4$ Hydro-fining
Run Number	26	26	187
Test Period	1	2	1
Conditions			
Recycle ratio	1.9/1	2.7/1	
Heater inlet			
Temperature, °F.	408	434	
Pressure, p.s.i.g.	400	460	
Heater outlet			
Temperature, °F.	910	920	
Pressure, p.s.i.g.	200	200	
Reaction chamber			
Temperature, ave., °F.	840	848	984
Temperature, max., °F.			1016
Temperature, furnace, °F.			875
Pressure, p.s.i.g.	200	200	600-605
Flash fractionator			
Feed, temp. °F.	792	793	
Flash chamber, °F.	768	762	
Reservoir, °F.	622	621	
12th tray, °F.	523	524	
Top, °F.	386	386	
P.D. receiver, °F.	80	62	
Column pressure, p.s.i.g.	56	64	
Receiver pressure, p.s.i.g.	55	62	
Absorber			
Wet gas, temp., °F.	80	62	
Dry gas, " , "	84	66	
Lean oil, " , "	99	98	
Rich oil, " , "	70	70	
Pressure, p.s.i.g.	54	61	
L.H.S.V.			5.0
Vc/Vc			12.5
Hydrogen rate, scf/bbl.			2000
Time on stream, cat., hrs.			2.5
Cat. deposit, wt. % catalyst			8.0

Table 30.--<u>Liquid product analyses, gasoline production by hydrofining heavy naphtha</u>

Type product	Thermally cracked naphtha	Residue	Light naphtha	Light gasoline	Heavy naphtha	Heavy gasoline	Blended gasoline
Sample #, RRS-	51-150	---	51-468	51-509	51-469	51-542	51-548
Sp. Gr., 60/60° F.	0.7626	1.0443	0.7077	0.7090	0.8311	0.7887	0.7324
Gravity, ° API	54.0	4.0	68.4	68.1	38.8	47.9	61.7
ASTM Dist., °F, at 760							
IBP	99	376	96	--	265	115	113
10%	158	597	135	--	315	187	154
50%	289	907	186	--	340	303	246
90%	384	--	233	--	391	376	358
EP	395	934	261	--	417	435	421
Rec. vol. percent	93.0	54.4	96.5	--	97.0	96.0	97.0
Res. vol. percent	1.1	--	0.8	--	2.2	1.0	1.0
Loss, vol. percent	5.9	--	2.7	--	0.8	3.0	2.0
Octane, F-2, motor, clear	66.8	--	70.0	--	66.0	67.6	68.9
+1 ml. TEL	70.1	--	73.6	--	69.8	76.0	74.6
+3 ml. TEL	72.8	--	76.8	--	72.3	81.2	79.3
Octane, F-1, research, clear	74.4	--	79.2	--	73.4	75.3	77.2
+1 ml. TEL	78.1	--	83.2	--	75.9	81.8	83.1
+3 ml. TEL	81.8	--	88.2	--	79.3	87.8	87.8
Hydrocarbon type, vol. %							
Paraffins	29	--	34	--	29	52	45
Naphthenes	3	--	8		6	0	2
Olefins	50	--	52	--	37	6	27
Aromatics	18	--	6	--	28	42	27
Tar Acids, vol. %	2.0	--	0.6	--	1.8	1.3	0.4
Tar bases, vol. %	10.2	--	2.2	--	8.7	6.2	2.2
A.S.T.M. gum, mg./100 ml.	45	--	3	--	1656	4.4	8.4
Cu. dish gum, mg./100 ml.	643	--	10	--	5034	23.9	23.2
Induction period, hrs.	0.25	--	8.08	--	0.25	+24	22
Doctor	sour	--	sour	sl. sour	sour	sweet	v. sl. sour
Corrosion	negative	--	positive	negative	positive		
Sulfur, wt. percent	0.68	0.56	0.26	0.19	1.06	0.02	0.13
Nitrogen, wt. percent	0.98	3.07	0.17	0.17	1.64	0.60	0.31
R.V.P., p.s.i. at 100° F.	12.7	--	--	--	--	--	--
Pour point, ° F.		80					
Flash, COC, ° F.		285					
Viscosity, SUS at 210° F.		257					
, SFS, at 122° F.		739					
Con. carbon, total oil, wt. %		18.32					

Gas analyses for this refining scheme are shown in table 31.

A variation of this refining process is shown in figure 9. The hydrogenation conditions, table 32, for the variation were slightly different. Catalyst temperature was decreased 40 degrees and reaction pressure raised 200 p.s.i. Properties of the gasoline are shown in table 33. The heavy gasoline produced under these changed conditions contained lower gum and sulfur but was inferior in octane number. Inhibitors were properly used in this heavy gasoline. Unfortunately, the light gasoline used for blending had too high an end point, and although inhibited, it contained sufficient gum to be detrimental to the blended gasoline. A comparison of data from tables 30 and 33 shows that if a better quality light naphtha had been used, gum contents of this finished gasoline would have been lower.

The octane numbers of the blended gasoline were low, primarily due to the increased pressure of hydrogenation. When the gasoline was blended with n-butane to ten p.s.i. Reid vapor pressure, octane numbers of the leaded samples were increased two to three numbers. Butane blending simulated the octane values that might be attained commercially.

Catalyst Life

Several runs have been made in an effort to establish the effective life of cobalt molybdate when processing heavy naphtha under optimum conditions for gasoline production. The results of one of these, run 216, are shown in table 34.

Run 216 was made in three stages. During the first stage, 52.5 volumes of oil were processed over a single volume of catalyst at a space velocity of 7.5. In each of the second and third stages, 45 volumes were hydrogenated over the same catalyst. There was an interval of several days between successive stages of the run, during which time the catalyst remained in position in the reactor at a temperature of 750° F. and under atmospheric pressure.

There was little significant change in the octane ratings of samples taken at various stages in the run. Other qualities of the gasoline produced throughout the run were acceptable for regular-grade gasoline with the exception of gum. The gasoline formed during the first stage of the run, however, contained less than specification gum so it is evident that the catalyst life was at least 52.5 volumes of oil per volume of catalyst.

The data indicate that the shutdowns between stages of the run had a significant effect on A.S.T.M. gum content. The gum was higher at the beginning of each stage than at the end. Although the phenomenon

Table 31.--Gas analyses, gasoline production by hydrofining heavy naphtha

Process	Recycle Thermal Cracking		$CoMoO_4$ Hydrofining
Test Period	1	2	1
Analyses, mol. %			
Hydrogen	5.1	6.1	73.6
Methane	39.6	46.9	11.2
Ethane	17.7	20.0	7.6
Propane	10.5	9.1	4.9
Butanes	3.9	1.2	1.6
Pentanes	1.3		0.4
Ethylene	3.3	3.7	
Propylene	6.2	5.3	
Butenes	3.8	1.6	0.2
Pentenes	1.6		
Hexenes	0.4		
Hydrogen Sulfide	2.3	1.8	
Carbon Dioxide	0.6	0.4	
Carbon Monoxide	3.7	3.6	0.3
Nitrogen			0.2
Avg. Molecular Weight	28.8	24.3	9.2

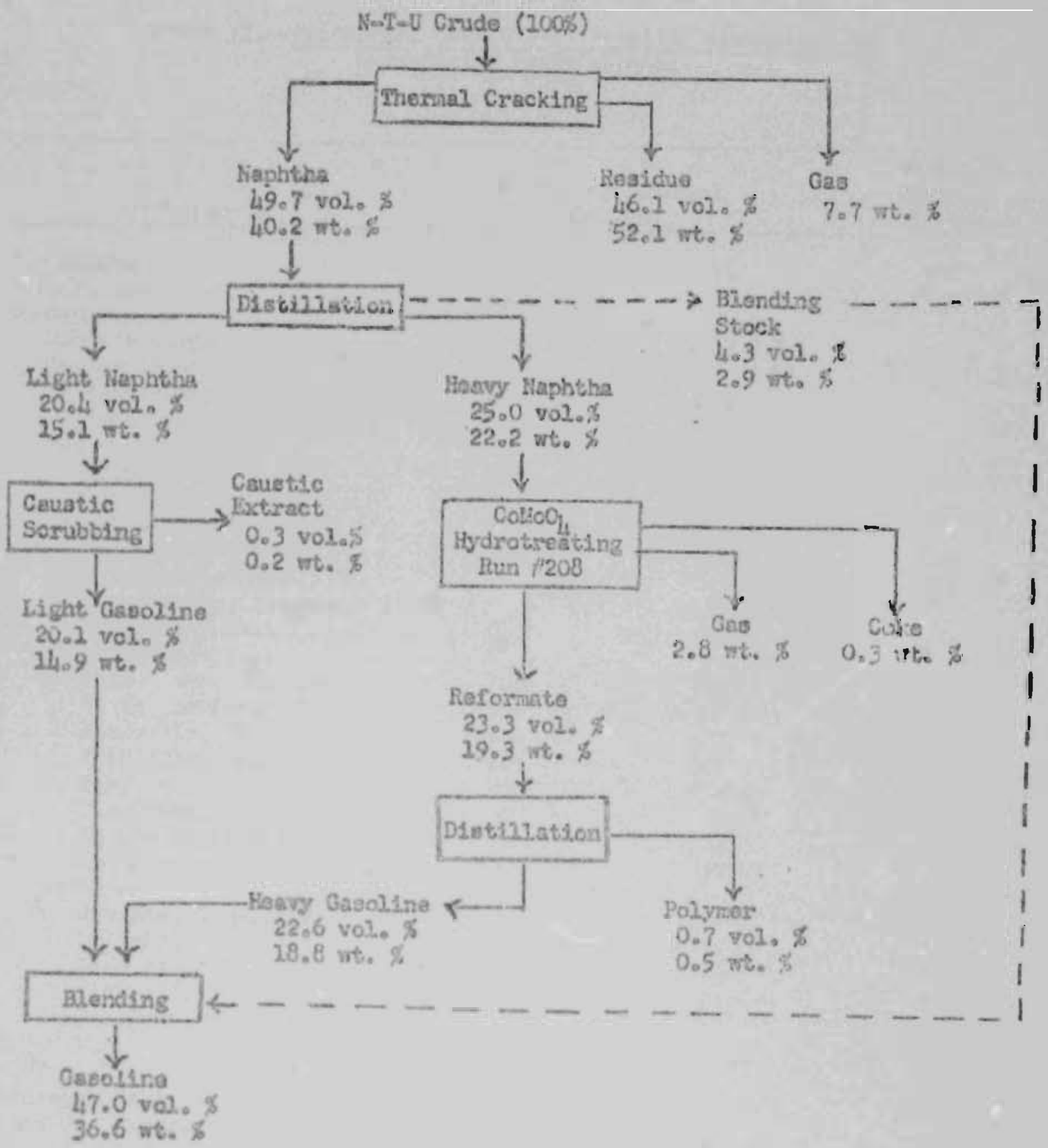

Figure 9.—Material Balances, Gasoline Production by Hydrofining Heavy Naphtha[1].

[1] No loss basis.

Table 32.--Processing conditions, gasoline production by hydrofining heavy naphtha

Process	Recycle Thermal Cracking		$CoMoO_4$ Hydro-fining
Run Number	26	26	208
Test Period	1	2	1
Conditions			
Recycle ratio	1.9/1	2.7/1	
Heater inlet			
Temperature °F.	408	434	
Pressure, p.s.i.g.	400	460	
Heater outlet			
Temperature, °F.	910	920	
Pressure, p.s.i.g.	200	200	
Reaction chamber			
Temperature, ave., °F.	840	848	942
Temperature, max., °F.			992
Temperature, furnace, °F.			850
Pressure, p.s.i.g.	200	200	800
Flash Fractionator			
Feed, temp. °F.	792	793	
Flash chamber, °F.	768	762	
Reservoir, °F.	622	621	
12th tray, °F.	523	524	
Top, °F.	386	386	
P.D. receiver, °F.	80	62	
Column pressure, p.s.i.g.	56	64	
Receiver pressure, p.s.i.g.	55	62	
Absorber			
Wet gas, temp., °F.	80	62	
Dry gas, " , "	84	66	
Lean oil, " , "	99	98	
Rich oil, " , "	70	70	
Pressure, p.s.i.g.	54	61	
L.F.S.V.			5.0
Vc/Vc			15
Hydrogen rate, scf/bbl.			2000
Time on stream, cat., hrs.			3
Cat. deposit, wt. % catalyst.			4.6

Table 33.--Liquid product analyses, gasoline production by hydrofining heavy naphtha

Type product	Thermally cracked naphtha	Residue	Light naphtha	Light gasoline	Heavy naphtha	Heavy gasoline	Blended gasoline
Sample #, HRS-	51-150	---	51-763R	51-763	51-764	51-799	51-800
Sp. Gr., 60/60° F.	0.7626	1.0443	0.7205	0.7200	0.8331	0.7786	0.7551
Gravity, °API	54.0	4.0	64.9	65.0	38.3	50.2	55.9
ASTM Dist., °F, at 760							
IBP	99	376	—	120	279	106	115
10% recovered	158	597	—	159	315	184	171
50% "	289	907	—	197	343	307	246
90% "	384	—	—	238	399	369	35[illegible]
EP	395	934	—	265	415	398	396
Rec., vol. percent	93.0	54.4	—	98.0	97.0	96.5	98.7
Res., vol. percent	1.1	—	—	0.5	2.5	0.6	0.5
Loss, vol. percent	5.9	—	—	1.5	0.5	2.9	0.8
Octane, F-2, motor, clear	66.8	—	—	67.1	69.4	62.1	65.3
+1 ml. TEL	70.1	—	—	71.5	72.2	70.0	70.4
+3 ml. TEL	72.8	—	—	75.0	73.8	76.0	1/ 74.6
Octane, F-1, research, clear	74.4	—	—	76.9	74.6	68.5	73.2
+1 ml. TEL	78.1	—	—	81.3	76.6	75.6	78.6
+3 ml. TEL	81.8	—	—	84.7	79.0	83.1	2/ 84.1
Hydrocarbon type, vol. %							
Paraffins	29	—	—	40	30	62	47
Naphthenes	3	—	—	4	5	0	4
Olefins	50	—	—	45	34	3	26
Aromatics	18	—	—	11	31	35	23
Tar Acids, vol. %	2.0	—	—	0.0	1.8	1.0	0.4
Tar bases, vol. %	10.2	—	—	0.6	10.0	4.0	2.4
A.S.T.M. gum, mg./100 ml.	45	—	—	7.8	2026.6	2.8	4.4
Cu. dish gum, mg./100 ml.	643	—	—	42.8	3006.2	17.9	37.8
Induction period, hrs.	0.25	—	—	4.92	0.25	24+	
Doctor	sour	—	—	sweet	sour	sweet	sour
Corrosion	negative	—	—	negative	positive	negative	negative
Sulfur, wt. percent	0.68	0.56	0.38	0.32	0.97	Nil	0.09
Nitrogen, wt. percent	0.98	3.07	0.14	0.12	1.71	0.43	0.30
R.V.P., p.s.i.a. at 100° F.	12.7	—	—	5.2	—	5.5	4.5
Pour point, °F		80					
Viscosity, SUS at 210° F.		257					
" , SFS at 122° F.		739					
Con. carbon, total oil, wt. %		18.32					
Flash, CoC, °F.		285					

1/ 77.3 when blended with n-butane (10% by volume) to 10 p.s.i.a. Reid vapor pressure.
2/ 85.9 when blended with n-butane (10% by volume) to 10 p.s.i.a. Reid vapor pressure.

Table 34.--Process conditions, material balances, and gasoline analyses for 19-hour run hydrogenating heavy naphtha

Volume oil/Volume catalyst	Charge	17.5	52.5	67.5	82.5	97.5	112.5	142.5
Process conditions:								
Pressure, p.s.i.		800						
L.H.S.V.		7.5						
Hydrogen rate, SCF/bbl.		3000						
Catalyst temp., °F.		958						
Stage		1		2			3	
Time on stream, hrs.		2.33	7.00	9.00	11.00	13.00	15.00	19.00
Material balances:								
Liquid product, vol. %		91.7						
Water, wt. %		1.2						
Catalyst deposit, wt. %		0.2						
Gas + loss, wt. %		11.4						
Gasoline, vol. %		84.2						
Gasoline analyses:								
Gravity, °A.P.I.	41.0	49.1	49.9	51.3	49.5	49.0	49.8	50.6
A.S.T.M. dist. °F. at 760								
IBP	250	126	118	124	118	122	119	112
10%	289	195	185	197	185	185	201	188
50%	332	291	285	289	292	297	292	289
90%	386	363	352	360	369	375	359	353
E.P.	418	390	375	381	391	389	376	375
Rec., vol. %	96.5	98.0	98.0	97.3	97.0	95.5	99.0	97.0
Res., vol. %	2.5	1.5	1.0	1.2	1.0	1.0	0.5	1.5
Loss, vol. %	1.0	0.5	1.0	1.5	2.0	3.5	0.5	1.5
Sulfur, wt. %	0.80	0.02	0.02		0.01	0.01	0.03	0.05
Nitrogen, wt. %	1.59	0.36	0.47		0.63	0.61	0.57	0.56
Paraffins, vol. %	32	54	52		46			49
Naphthenes, vol. %	7	5	9		8			8
Olefins, vol. %	38	2	6		8			8
Aromatics, vol. %	23	39	33		38			35
Octane, motor, clear	67.6	61.6				63.9	62.9	64.5
Octane, motor, + 1 ml. T.E.L.	70.3	70.0				72.7	70.8	72.2
Octane, motor, + 3 ml. T.E.L.	72.8	77.0	77.2		78.7	78.4	77.3	79.5
Octane, research, clear	76.8	68.0				70.7	69.2	71.9
Octane, research, + 1 ml. T.E.L.	79.1	76.6				77.8	76.3	79.1
Octane, research, + 3 ml. T.E.L.	82.3	82.8				84.9	83.7	85.5
Gum, A.S.T.M., mg/100 ml.	1708	4.6	1.4	15.4	19.4	12.0	24.2	9.6
Gum, cu. dish, mg/100 ml.	2972	1/19.8	1/11.2	1/20.9	1/54.4	1/24.6	1/46.0	1/25.5
Induction period, hrs.		1/24	1/24			1/24		1/24
Tar acids, vol. %	0.4	0.6	0.0		0.9		0.0	0.0
Tar bases, vol. %	13.8	4.3	5.5		5.3		6.3	6.0

1/ Inhibited with 0.032 lbs. U.O.P. #5/bbl.

of decreasing gum during the progress of the run had not been observed previously, there is no reason to believe that the data are in error. On the other hand, it should not be concluded that the longer the run, the less gum is contained in the gasoline. It is more likely that the conditions prevailing at the beginning of the run were not as favorable for gum elimination as the conditions which became standardized as the run progressed. In other words, when temperature, feed rate, hydrogen rate, hydrogen partial pressures, and reaction gas pressures achieved the proper equilibrium for hydrofining, the best gum-elimination conditions were obtained. During this period of adjustment, the catalyst probably picked up a certain amount of coke which reduced its effectiveness. Consequently, each start-up probably caused an initial coke laydown which successively rendered each stage less effective. It is logical to believe, therefore, that more than 52.5 volumes of specification quality naphtha would have been produced if the run had been operated continuously.

Other runs which contributed data in the study of catalyst life clearly indicated that the operating variables used played an important part in the length of catalyst life. Increasing temperature decreased catalyst life, and increasing pressure and hydrogen feed rate prolonged activity.

Conclusions

The data shown in the previous tables are sufficient to determine the influence of changes in operating conditions upon hydrogenation of heavy naphtha.

These conclusions are:

1. As the reaction temperature is increased between 950° and 1010° F.:
    - a. Gas and coke formation increase.
    - b. Liquid recovery is lowered, the decrease becoming rapid at temperatures over 980° F.
    - c. Hydrogen consumption is not greatly altered.
    - d. Sulfur removal is slightly greater.
    - e. Nitrogen removal is more difficult.
    - f. Clear octane ratings are increased.
    - g. Sensitivity is increased.
    - h. Lead susceptibility is lowered.
    - i. Gum content is lowest near 980° F.
2. As the pressure is increased from 200 to 800 p.s.i :
    - a. Catalyst deposit is decreased and catalyst life increased.
    - b. Hydrogen consumption is increased.

c. Liquid recovery is not greatly affected when processing at elevated temperatures.
d. Sulfur and nitrogen contents of the products are decreased.
e. Gum contents are decreased.
f. Clear octane numbers are decreased.
g. Lead susceptibility is increased.
h. Olefin content and sensitivity are decreased slightly.

3. As the hydrogen flow rate is increased from 1,000 to 4,000 standard cubic feet per barrel:

a. Catalyst deposit is decreased and catalyst life increased.
b. Hydrogen consumption is increased.
c. Sulfur content of product decreases rapidly between 1,000 and 2,000 cubic feet of hydrogen.
d. Nitrogen content decreases.
e. Gum content decreases.
f. Clear octane ratings and sensitivities are not materially affected.
g. Lead susceptibilities are improved.

4. As the space velocity is increased from 2.5 to 10.0 volumes of oil per volume of catalyst per hour:

a. Hydrogen consumption is not affected.
b. Catalyst deposit is lowest at a space velocity of 7.5.
c. Liquid recovery and gasoline production are highest at space velocities from 5.0 to 10.0.
d. Gas production is higher at the lower space velocities.
e. Sulfur removal is greatest at a space velocity of 5.0.
f. Nitrogen removal is greatest at space velocities from 2.5 to 7.5.
g. Gum content is lowest at space velocities of 5.0 and 7.5.
h. Clear octane numbers are lowest and lead susceptibilities highest at space velocities of 5.0 and 7.5.
i. Octane sensitivity is not affected.

Optimum conditions for the hydrogenation of heavy naphtha have been selected. They are:

1. Catalyst temperature - 950° to 980° F.

2. Reaction pressure - 600 to 800 p.s.i.

3. Hydrogen flow rate - 2000 to 3000 SCF/bbl.

4. Space velocity - 5.0 to 7.5 Vo/Vc/hr.

Light naphthas suitable for blending with the hydrogenated heavy gasoline should have several important characteristics. These are:

1. Gum content should be less than specifications.
2. Octane ratings should be higher than specification minimums.
3. Olefin content should be high. Light naphthas with 50 percent olefins will give good sensitivity when blended with hydrogenated gasolines.
4. The naphthas should be doctor sweet.
5. Other properties will be such that when blended with a given heavy gasoline, the blend will meet desired specifications.

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APPENDIX

Heats of Hydrogenation

Heats of hydrogenation for typical runs charging coker distillate, whole naphtha, and heavy naphtha were calculated based on heat balances drawn around the unit. Heat balances were determined by substracting the sensible heat contents of the reactants (oil and hydrogen) as they entered the catalyst bed from the sum of the sensible heat contents of the products leaving athe catalyst bed plus the heat lost through the walls of the catalyst chamber. Heat contents of the shale-oil fractions were determined by using published heat values for petroleum fractions. Heat losses by conduction through the catalyst bed were based on an over-all heat transfer coefficient of 8.0 determined from experimental values.

The results of these calculations are tabulated below. These values represent the net heat of reactions consisting of hydrogenation followed by pyrolysis. The data indicate that the heavier the charge stock, the less the heat of hydrogenation.

Charge stock Run No.	Coker distillate 213	Whole naphtha 177	Heavy naphtha 198
Hydrogenation conditions			
Furance temperatures, °F.	825	850	850
Catalyst temperature, °F.	855	961	947
Outlet temperature, °F.	829	931	945
Reaction pressure, p.s.i.	1000	600	600
L.H.S.V.	1.0	5.0	5.0
H_2 flow, SCF/bbl.	2000	2000	2000
Heat of hydrogenation B.t.u./lb. of charge	243	292	265

END

of

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