Part of report
reel # 1
Item 65

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Dr. Michael Ludwigshaven July 1, 1941

Conference on Progress in CO-H_2 Synthesis

Fe catalysts operating over 300°C cannot be used in regular tubular converters and in range 300-350°C carbon deposition may occur.

The gas recycle process was developed using smaller heat exchange surfaces than in Rührenofen, and outside heat exchanger permitting higher temperature drop (up to 50°) across heat exchanger surfaces. At reaction temperature 300°C 2/3 to 3/4 of the liquid product was gasoline. After removal of O_2 compounds with clay a research octane number of 84-85 was obtained, highly olefinic. After bleaching earth (Fuller's earth) refining and addition of a naphthol as stabilizer would be stored without gum deposition. About 1/6 of liq. prod. was diesel oil containing 1½% O_2 with cetane no. 50-55 1% paraffin obtained. 30% of total hydrocarbon yield was C_2 C_3 C_4 largely olefinic.

In experiments in a 800 - 1000 ton/yr recycle oven turbulence was observed in passing for narrow pipes into converter - New designs should be such as to eliminate this.

For gas recycle work mechanically tough sintered Fe cats. necessary. catalysts are too friable.

For "Middle oil production" the "Schaufahrweise" technique was used. An Fe powder ex. carbonyl ground in oil operated at 240-250°C gave good yield of better middle oil than gas recycle process. A minimum of olefins was aimed at. The diesel cetane number was 60-70. This Schaufahrweise has the advantage of very low gaseous hydro prod. 3-8% (varying with reaction temperature as against 18-20 by gas recycle. Operation may be conducted in Ruhr, but it is simpler to use "Schaumplatte" which makes settling out of catalyst less troublesome. Outside heat exchange may be employed. Possible product distribution.

Gasoline	Middle Oil	Paraffin
30	30	40
60	30	10

Gasoline obtained by operation at 310°C had a research octane of 90.

Operating data on gas recycle

Reaction temperature. 325°C.

RESTRICTED

Yield (STY) 0.8 kg Prod/liter of Catalyst/day
Conversion 91.5% in 2 stages
Yield/cu.meter ideal gas 160 gms.
70% of product - 112 gms. was liquid
% of the total product 7% alcohols and acids
15% Diesel oil 200-350°C
48% Gasoline to 200°C
30% of product ~~of total~~ = 48 gms. was gaseous
~~prod. 48% gas was gaseous~~
of total prod. 7% C_2H_4
9% C_2H_6
3% C_3H_8
6% Butylenes
2% Butane.
100%

60-65% of the C_4 was Iso, including polymerisation of lower olefins The liq. yield was 142 gms rather than 112 g. The 48% of gasoline can be freed of O_2 and made colorless by clay refining with drop from 48% to 45%.

Operating data on Schaumfahrweise

Reaction temperature	240-250°
Yield STY	0.2 kg/liter of Shaumvol/day
Conversion	90% in 3 stages
Yield gas/Nm^3	170 gms liq - solids
of which 4-5% was alcohol contained in H_2O produced	
Liquid oils	30% Gasoline, 30% middle oil 40% paraffin
Gasol 4-5%	
CH_4 ~~3%~~ 3%	

To obtain hi,h octane gasolin as main product of Schaumfahrweise (S.F.), temperature of 310° desirable. The yield is then 160 gms.

	Schaumfahrweise Sump Phase	Gas Recycle Gas Phase
React. Temperature	250°	195°
Catalyst	Michael Fe-Sintered	Hersebung Holten Fe - in ~~Mie~~ Mie Reduced
Alcohols	Maximum at 160°	Max. 36% in one Fraction
In the Washing Media Fraction C_8 to C_{18}	not over 12%	26 - 28%
Olefins in C_4-C_{18}	~~45%~~ 45%	40 - 45%

Sum of alcohols and olefins approximately constant.

Dr. Wensel reported that Leuna had recently obtained a product having 80% olefins in the C_8-C_{18} fraction.

Dr. Michael reported briefly on experiments with Hersebury Synol catalysts according to B.F. at 20 atmospheres and 210°C. With STY 0.15 product as follows:

	220-250	250-300	300-350
Alcohols	23	24	15
Olefins	36	30	27

II Oil The Recycle Process Dr. Duftschmidt, Oppau.

In 1934 liquid phase experiments with Oil Recycle oil and gas cocurrent on a fixed catalyst. Apparently operation is in "boiling phase" maintained by recycling relatively light boiling ends. Later operation at 100 atmospheres in 2 stages.

At 240° entering and 290° leaving converter and 50% conv in one stage, with 150g. liquid and gasol for 2 stages :-

40% primary gasoline	O.N - 62 - 68 clear O.N + 0.1 Pb 85 2% O_2 (removable by H_2O wash).
20% middle oil	cetene No. 78
20% Hard Wax	M P + 95
15% Gasol (mC_2)	85% olefin
5% alcohol	25% Methanol 50% C_2H_5OH 25% higher alcohols acetaldehyde, aceton, etc.

STY is 30 g/l. catalyst/hr = 0.76/liter catalyst/day

With increasing pressure (experiments at 25-100, 150 and 180 atmospheres) the O_2 content of product increased, at 180 atmospheres, large amounts of low boiling and only minor amounts of high boiling alcohols obtained. To obtain chiefly alcohols it is necessary to operate at small conversions and with high H_2 synthesis gas. At CO/H_2 ratio of 1:1 180 atmospheres, and 280° - 290°C with 28 - 30% conversion, 48.5% alcohols were obtained :- 8.5% CH_3OH, 21% C_2H_5OH, 10% C_3H_7OH, 6.5% C_4-C_{11} alcohols and 2 to 5% C_{12}-C_{20} alcohols. The 33.5% ketone contained 26.5% gasoline, 3.5% middle oil, 3.5% over 300°C. The 18% fatty acids were 11% H_2O soluble 5% C_5 to C_{11}, 2% C_{12}-C_{20}. Alcohols disappeared from product at high conversions and when C was deposited on contact.

II Wax-Synthesis Dr Schneiderwirth Ammonia Lut, Oppau.

Ruhrchemie equipment cobalt catalysts
CO/H_2 1:2, 12 atmospheres Previously reported

Later Fe catalysts developed, active at 230° C and lately active at 195°C.

In 1 stage 70-75 gms. product/Nm^3, 10% paraffin 15% middleoil, 15% gasoline, (3-5% alcohols and 6-10% acids)
Cale. yield on 100% converter 130-140 gms/Nm^3

At 260°C with molten Fe catalyst 75-80% olefins of which 15-30% are useful in OXO synthesis containing 90-95% straight chains.

IV Wax and Synol Synthesis Dr Wenzel, Merseburg

In 1938 the high cost of F.T. Ruhrchemie primary product stimulated a search for processes to make special products.

1) Hard Wax A $Co-Al_2O_3-ZnO$ catalyst was developed which at 180-185°C and 10 atmospheres in tube converter in 1 stage yielded 140 gms/Nm^3 of which 70% was hard wax 95°C m.pt.

2) Alcohols Synthesis ammonia catalysts (Molten Fe) yielded in various fractions.

	% alcohols	% olefins
100 - 200	60	30-20
-300	65	30-20
-400	32	35-40

The liquid must be acidified to avoid esterfication during distillation. 85% of alcohols olefins straight chain.

Comparison of two modes of operation with Synthesis Ammonia Catalysts.

	Gasoline + Diesel Oil 3 stages	Alcohols (Synol) 4 stages
CO_2 absorption	2 times	3 times
Gas - Belastang m^3/gas/m^3 catalyst /hr	1:250	1:150
STY tons fluid product/m^3/day	0.92	0.64
Temperature	220-245	190-220
Gas liquid product/Nm^3	140	160
" gasol Nm^3	14	16
Total gas/Nm^3	154	176
" " " including CH_4	181	190
% CH_4 (on feed gas)	8	5

Product composition	%	Alcohols	%	alcohols
to 200	64-40	5-10	44	38
200-300	18-30	3-8	18	56
300-400	6-15	2-5	15	50-60
400	12-15	2-5	23	37

Ruhrchemie converters may be used. The molten Fe catalyst is easy to prepare, very hard and stable and can be readily regenerated by fusion.

To produce higher alcohols it is essential:-
1) To use low temperatures and pretreat catalyst with H_2
2) To use low conversions (the alcohols are decomposed at higher temperatures.
3) Low contact time not more than 2 m. catalyst depth.

Co_2 washing in between stages done with H_2O under pressure CO_2 dropped from 15 to 3%. CO_2 scrubbed with active char to recover light hydrocarbons.