UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL
LOUISIANA, MISSOURI

1461

From Dr. M. Pier's File T-436

W. M. Sternberg
January 12, 1948

High Pressure Experiments
Ludwigshafen, 558

August 27, 1941
Schmd./R

COMPARISON OF PRODUCTS OF VAPOR PHASE AND FOAM PHASE SYNTHESES AT DIFFERENT TEMPERATURES

Table 1	Synol products from Leuna with no pretreatment.
Table 2	Synol products from Leuna de-acidified before distillation.
Table 3	Products from straight vapor phase reactors at 195°C, experimental conditions as in 1 (Leuna) no pretreatment.
Table 4	Products of straight vapor phase reactors at 195°C, experimental conditions as in 2 (Leuna), de-acidified before distillation.
Table 5	Products from gas circulation reactors with a normal thruput at 195°C, no pretreatment.
Table 6	Products from gas circulation reactors with a short residence time at 195°C, no pretreatment.
Table 7	Products from circulation reactors with short residence time at 195°C, de-acidified before distillation.
Table 8	Products from stirred foam reactors temperature 210°C, no pretreatment.
Table 9	Repetition of table 8.
Table 10	Products of stirred foam reactors temperature 210°C, de-acidified before distillation.

Table 11 Products of stirred foam reactors temperature 250°C, de-acidified before distillation.

Preliminary Report

Before a final judgement on the value of our synthesis oil process for the production of synol can be given, the results of a few outstanding tests and their comparison of the results of the tests of synol products from Leuna must be obtained.

The original products and the products freed from acid before distillation have been investigated. According to Dr. Reisinger, analysis does not include alcohols as such as the products are not freed from acid before testing.

Differences are not very great according to our investigations, presumably because some of the alcohols were lost in the washing. Work is still continued to find out to what extent this is true.

The following results can be found from comparison of the original synol products (table 1 from Leuna) with the products from our small Fischer reactor (table 3) and with the products from gas circulation reactors (table 5, 6, and 7).

The free alcohol content of the middle oil fraction is around 25 percent on the average in the Leuna product and 20 percent in our product from the Fischer reactor;

they amount to 15 percent in the products from our gas circulation furnaces with a longer time of residence, 15 percent with a shorter time of residence, and 18 to 20 percent after a previous de-acidifying of the products.

The total alcohol content in the Leuna product is 29 percent, 35 percent in the Fischer reactor, 24 percent in the gas re-circulation reactors with a long residence time, 22 percent with a short residence time and 29 percent after a previous de-acidifying.

We may make the following preliminary statement: The difference between the straight passage and the circulation reactors is slight. The former are however, better adapted for the synthesis of synol. We could give no information of the contents of the higher alcohols such as reported by Dr. Wenzel. Analyses made in Leuna are not available. We have, however, requested some products for investigation and asked for a testing by the Leuna method. There are, however, no fundamental differences in the products investigated in both places.

The products of the stirred foam reactors at 210°C containing 12 percent of free alcohols before being de-acidified, with 29 percent total alcohols, and after being de-acidified 20 percent free alcohols

and 28 percent total alcohols.

The products from the foam reactors at 250°C (method of operations for middle oil production) contain 11 percent free alcohols after de-acidifying and 14 percent total alcohols in the middle oil fraction.

The olefin content is always the higher the ower the alcohol content.

The sum of olefins and alcohols is higher in the products of our method of synthesis than in the synol products from Louna.

Experiment No. 717
Leuna Product
May 21, 1941

Table 1

Leuna Synol Products not Pretreated

Fraction	A -100°	B 100-150°	C 150-200°	D -100°/2mm	E -150°/2mm	F -200°/2mm	G -250°/2mm	H Residue
Proportion	19.4%	18.2%	19.2%	7.8%	14.6%	10.9%	4.5%	6.4%
	Gasoline 56.8%			Middle Oil 36.8%				
Mol. weight	80	101	112	143	190	259	265	580
Free alcohols	7.5%	21.8%	24.0%	14.6%	20.0%	26.1%	19.0%	-
Esterified alcohols	0.3%	0.6%	1.0%	2.2%	4.5%	7.3%	6.3%	13.0%
Total alcohols	7.8%	22.4%	25.0%	16.8%	34.5%	33.4%	25.3%	-
Aldehyde +Ketones	8.7 %	11.8%	4.1%	3.7%	3.5%	2.3%	1.6%	
Free acids	0.60%	0.6%	0.6%	0.1%	0.1%	0.1%	0.3%	
Olefins (hydrogenat. No.)	44.8%	30.5%	21.8%	27.2%	23.4%	19.0%	13.7%	9%
Iodine no. (Hanus)	51.0%	30.5%	22.6%	28.6%	26.0%	22.6%	19.8%	41%

Experiment No. 719 -6- T-436
75 cm reactors
May 26, 1941

Product from Straight Vapor Phase Reactors Table 3

Catalyst: Fused catalyst (Leuna) Temp. 195° 20 atm
Conversion 20 - 30 percent space-time yield 0.2
Products not pretreated

	A	B	C	D	E	F	G	H
Fraction	-100°	100-150°	150-200°	-100°/3mm	-150°/2mm	-200°/2mm	-250°/2mm	Residue
Proportion	27.4%	15.3%	12.7%	7.8%	16.8%	10.3%	4.7%	5%
	Gasoline 55.4%			Middle Oil 39.6%				
Mol. weight	83	95	116	149	206	249	306	800
Free alcohols	22.2%	24.0%	24.0%	24.0%	21.3%	14.7%	21.5%	11.5%
Esterified alcohols	2.1%	0.7%	5.0%	9.1%	15.0%	20.0%	28.0%	41.0%
Total alcohols	24.3%	24.7%	29.0%	33.1%	36.5%	34.7%	49.5%	52.5 %
Aldehyde + Ketones	24.8%	16.5%	8.9%	7.4%	4.6%	5.1%	7.1%	68.0%
Free acids	0.15%	4.1%	2.7%	0.1%	0.1%	0.1%	0.2%	0.5%
Olefins (hydrogenat. no.)	33.0%	22.2%	17.5%	20.6%	14.7%	9.2%	12.2%	
Iodine no. (Hanus)	45.0%	19.4%	20.7%	25.0%	18.0%	18.0%	26%	

T-436
Table 5

Experiment No. 716
U-reactor 2
May 20, 1941

Products from Gas Circulation Reactors

Catalyst: Fused, finely ground (Leuna) Temp 195° 20atm
Conversion abt. 50 - 60% space-time yield 0.4 norm. residence time
Product not pretreated

	A	B	C	D	E	F	G	H
Fraction	-100°	100-150°	150-200°	-100°/5mm	-150°/2mm	-200°/2mm	-250°/2mm	Residue
Proportion	11.7%	8.9%	9.8%	3.9%	14.6%	14.5%	6.4%	30.9%
	Gasoline 30.4%			Middle Oil 38.8%				
Mol. weight	74	91	123	162	193	246	292	560
Free alcohols	15.4%	27.5%	24.1%	19.0%	13.2%	9.4%	16.7%	15.0%
Esterified alcohols	1.2%	2.0%	3.5%	6.0%	7.2%	8.5%	13.0%	19.0%
Total alcohols	16.6%	29.5%	27.6%	25.0%	20.4%	17.9%	29.7%	34.0%
Aldehyde + Ketones	6.6%	9.5%	4.4%	5.4%	3.2%	3.1%	6.8%	26.0%
Free acids	0.6%	6.1%	4.9%	0.8%	0.5%	0.3%	0.4%	0.6%
Olefins (hydrogenat. no.)	46%	39%	47%	48%	34%	21%	28%	6.5%
Iodine no. (Hanus)	53%	32%	47%	42%	34%	28%	39%	41%

Oxygen was not determined

Table 6

Experiments No. 724
U-Reactor 2
June 25, 1941

Product from Gas Circulation Reactors

Catalyst: Fused catalyst (Leuna) Temp 195°, 20 atm,
abt 20% gas yield 0.2 space-time yield short residence time
Product not pretreated

	A	B	C	D	E	F	G	H	I
Fraction	-100°	100-150°	150-200°	-100°/2mm	-150°/2mm	-200°/2mm	-250°/2mm	-275°/2mm	Residue
Proportion	16.2%	16.4%	13.2%	8.4%	10.4%	8.0%	5.9%	2.4%	19.5%
		Gasoline 45.8%			Middle oil 32.8%			Solids 22.0%	
Mol. wt.	79	90	127	173	198	244	283	327	700
Free alcohols	43%	30%	28%	29%	18.0%	8.7%	16.0%	15.4%	11%
Esterified alcohols	1.3%	1.6%	3.5%	6.5%	11.0%	15.3%	15.0%	13.9%	23.4%
Total alcohols	44.3%	31.6%	31.5%	35.5%	29.0%	24.0%	31.0%	29.3%	34.4%
Aldehyde + Ketones	7.3%	7.3%	4.4%	3.8%	3.8%	3.7%	4.5%	3.8%	49.0%
Free acids	0.5%	3.6%	2.0%	0.3%	0.2%	0.2%	0.2%	0.3%	0.5%
Olefins (hydro. no)	5%	41%	44.5%	42.5%	34.5%	30.0%	14.5%	18.4%	-
Iodine no. (Hanus)	5%	42.5%	44.5%	51.0%	42.5%	38.0%	33.6%	35.6%	45%
Oxygen	6.7%	8.6%	7.8%	5.0%	4.7%	3.6%	3.4%	3.3%	2.9%

T-436
Table 7

Experiment No. 720
U-reactor 1
July 28, 1941

Products from Gas Circulation Reactors

Catalyst: Fused catalyst (Leuna) Temp. 195° 20 atm
abt. 15 % conversion 0.2 space-time yield short residence time
Products deacidified with 5% KOH before distillation, washed 4 times

	A	B	C	D	E	F	G	H
Fraction	-100°	100-150°	150-200°	-100°/18mm	-150°/18mm	-200°/18mm	-250°/18mm	250°
Proportion	6.6%	22.6%	18.8%	3.4%	13.4%	23.3%	6.7%	5.2%
		Gasoline 48.0%			Middle oil 46.8%			
Mol. weight	95	108	121	131	162	216	291	460
Free alcohol	7.8%	19.0%	28.7%	24.1%	28.5%	19.0%	13.8%	15.0%
Esterified alcohols	0.4%	0.8%	2.3%	2.7%	3.2%	3.8%	5.2%	16.2%
Total alcohol	8.2%	19.8%	31.0%	26.8%	31.7%	22.8%	19.0%	31.2%
Aldehyde + Ketones	5.7%	6.7%	9.0%	7.6%	6.5%	4.2%	7.8%	92.0%
Free acids	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%
Olefins (Hydro. No.)	65%	59%	46%	46%	38%	23.5%	46%	13%
Iodine no. (Hanus)	65%	52%	34.5%	35.5%	29%	20%	20%	48%
Oxygen	4.2%	5.6%	7.2%	6.0%	5.3%	2.8%	2.3%	4.7%

Table 8

Experiment No. 720
U-reactor 5
June 4, 1941

Products from Stirred Foam Reactors

Catalyst: Powdered fused catalyst (Leuna) Temp. 210° 20 atm. abt. 20% conversion space-time yield 0.15 from 12 days run. Product not pretreated.

Fraction	A -100°	B 100-150°	C 150-200°	D -100°/2mm	E -150°/2mm	F -200°/2mm x)	G Residue
Proportion	10.5%	8.1%	10.1%	6.2%	12.1%	47.9%	5.1%
	Gasoline 28.7%			Middle oil 66.2% x)			
Mol. wt.	80	91	117	133	175	259	440
Free alcohols	17.5%	15.2%	18.2%	22.6%	23.8%	14.8%	7.8%
Esterified alcohols	2.3%	3.0%	6.5%	9.1%	14.3%	17.0%	35.0%
Total alcohols	19.8%	18.2%	24.7%	31.7%	38.1%	31.8%	42.8%
Aldehydes + Ketones	14.9%	9.2%	10.9%	9.4%	7.0%	4.7%	94.0%
Free acids	0.7%	6.3%	3.4%	0.5%	0.4%	0.1%	0.9%
Olefins (Hydro. no)	47%	30%	39.6%	35.8%	30.0%	27.5%	
Iodine no. (Hanus)	46%	34%	37%	36%	33.7%	29.7%	44.5%
Oxygen	11.18%	13.6%	10.46%	7.49%	6.52%	4.53%	6.97%

x) The large size of this fraction must be explained by a partial carrying over of the liquid phase. Test was repeated at a later date, Experiment 725.

Table 9

Experiment No. 725
U-reactor 5
June 28, 1941

Products from Stirred Foam Reactors

Catalyst: Powdered fused catalyst (Leuna) Temp 210 20 atm
Repetition of experiment 720, after 5 weeks operation
Product not pretreated

Fraction	-200°	A -100°/2mm	B -150°/2mm	C -200°/2mm	D >200°/2mm
Proportion Gasoline	46.5%	6.4%	12.9%	20.6%	13.6%
			Middle oil 39.9%		
Mol. Wt.		161	202	271	600
Free alcohols		16.3%	10.0%	9.0%	13.2%
Esterified alcohols		15.0%	21.0%	18.8%	52%
Total alcohols		31.3%	31.0%	27.8%	65.2%
Free acids		0.5%	0.3%	0.3%	2.7%
Aldehydes + Ketones		7.8%	3.7%	2.0%	48.0%
Olefins (Hydro. no.)		39.0%	27%	15.2%	-
Iodine no. (Hanus)		43.0%	34%	26%	50%
Oxygen		6.52%	5.66%	4.10%	5.79%

Table 10

Experiment No. 730
U-reactor 3
August 4, 1941

Product from Stirred Foam Reactors

Catalyst: powdered fused catalyst Temp. 210° 20 atm
Product deacidified before distillation with 5% KOH, washed 4 times

	A	B	C	D	E	F	G
Fraction	-100°	100-150°	150-200°	-100°/1mm	-150°/1mm	-200°/1mm	> 200°/1mm
Proportion	7.2%	13.7%	14.4%	11.0%	15.0%	25.2%	13.4%
	Gasoline 35.3%			Middle oil 51.2%			
Mol. wt.	84	97	134	158	202	261	635
Free alcohols	8.0%	14.6%	24.0%	21.0%	19.5%	8.8%	-
Esterified alcohols	8.2%	15.3%	27.4%	28.5%	34.1%	25.4%	-
	0.2%	0.7%	3.4%	7.5%	14.6%	16.6%	45%
Aldehydes + Ketones	6.0%	6.2%	9.2%	6.8%	5.8%	3.9%	95.0%
Free acids	0.01%	0.03%	0.03%	0.05%	0.03%	0.05%	0.05%
Olefines (Hydro. no).	62%	57%	55%	54%	43.5%	32.0%	
Iodine No. (Hanus)	63%	56%	50%	49%	41.3%	30.7%	63%
Oxygen	4.63%	5.72%	6.67%	5.42%	5.05%	2.25%	6.56%

T-436
Table 11

Experiment No. 731
U-reactor 6
August 14, 1941

Products from Stirred Foam Reactors

Catalyst Fe_2O_3 (red iron oxide catalyst) Temp 250° 20 atm
Product deacidified with 5% KOH before distillation and washed 4 times.

Fraction	A -100°	B 100-150°	C 150-200°	D -100°/8mm	E -150°/8mm	F -200°/4mm	G +200°/4mm
Proportion	20.6%	5.9%	16.9%	6.1%	10.8%	15.7%	24.2%
	Gasoline 43.4%			Middle oil 32.5%			
Mol. Wt.	81	97	115	140	180	237	445
Free alcohols	3.5%	9.9%	13.0%	12.0%	11.0%	8.2%	5.2%
Esterified alcohols	0.7%	0.8%	1.2%	1.7%	3.0%	6.2%	8.2%
Total alcohols	4.2%	10.7%	14.2%	13.7%	14.0%	14.4%	13.4%
Aldehydes + Ketones	3.6%	2.6%	3.9%	4.1%	3.7%	2.9%	95.0%
Free acids	0.04%	0.5%	1.2%	0.9%	1.4%	0.7%	2.5%
Olefins (Hydro. no.)	69%	61.5%	60.0%	62.0%	54.5%	55.0%	-
Iodine no.	70.5%	60.5%	59.0%	63%	56.3%	59.5%	44.0%
Oxygen	3.02%	3.94%	4.01%	2.91%	-	-	-