Leuna Works - March 27, 1944

MEMORANDUM ON THE FIRST OPERATING PERIOD OF THE AROBIN REACTOR

Large-scale experiments were carried out in a reactor of 1.6 feet diameter provided with 4 connections for the injection of cold gas. The catalyst filling of the reactor was 31 cubic feet. Catalyst 6853, activated aluminum silicate with 1% molybdic acid, in the shape of spheres was used; 31 cubic feet of catalyst (1,515 pounds) were placed into the reactor. The operating pressure was 2,940 psig. The attached flow sheet indicates the operation of the process.

In order to test the safety of the apparatus and the activity of the catalyst, the unit was operated on separator product from the pre-hydrogenation. The feed rate was 185 gallons of oil per hour which is equal to a space velocity of 0.8 volumes of feed per volume of catalyst per hour. The conversion was 45 - 50% - i.e., 45 - 50% of the feed was cracked. The non-reacted portion was separated from the product by distillation and recycled. The determination of the conversion was carried out by means of distillation, the portion boiling up to 329°F. being considered as product. The reaction is exothermic and the operating data indicate a heat of reaction of about 612 B. t. u. per pound of feed stock. The feed was preheated in such a way that the reactor inlet temperature was 725°F. This resulted in a temperature of 770°F. in the first third of the reactor. By the addition of cold gas (17,640 cubic feed per hour at the space velocity given above), the temperature in the other parts of the reactor was kept at 797°F.

After 88 tons of separator product from the pre-hydrogenation had been processed, the unit was changed over to the hydroformer bottoms from the Moosbierbaum plant. (This material was obtained by hydroforming Roumanian straight-run gasoline.) The through-put under these conditions was 211 gallons per hour of feed stock per 31 cubic feet of catalyst, corresponding to a space velocity of approximately 1 : 1; the conversion under these conditions was about 50%. The amount of gas recycled was 194,100 cubic feet per hour and the amount of cold gas was 21,100 feet per hour. The reactor inlet temperature was kept at 734°F. and the maximum temperature in the last part of the reactor was kept at 797°F.

The unit was operated under these conditions for about 1 month after which time the feed rate was reduced to 145 - 159 gallons per hour due to lack of feed stock. After a total operating time of about 8 weeks, the unit had to be shut down since no raw material was available. During the last three weeks of operation the ratio of recycle gas to liquid feed product was changed and only 141,000 cubic feet of recycle gas and 24,700 cubic feet of cold gas were used.

In order to maintain the conversion at 50%, the reactor temperature had to be raised to 815°F. Subsequently, the space velocity was again raised to 1 : 1. However, after an operating period of 2 weeks, the space velocity had to be reduced again to 1 : 0.625. This space velocity was then maintained for another 3 weeks. Towards the end of the operating period the reactor temperature had to be raised to 824°F. in order to maintain a conversion of 50%. During the total period of 130 operating days, 88 tons of separator product from the preliminary hydrogenation and 615 tons of Arobin were processed. The unit had to be shut down about 20 times because of air raid alarms. The procedure followed in these cases consisted of shutting off the liquid feed as soon as an "alert" was sounded and the reactor was run dry with recycle gas until the actual danger signal was given. At that time the circulating pump was shut off and the reactor remained under pressure but

without gas or product circulation. However, it happened several times that the two commands followed each other so fast that this practice could not be followed and it must be assumed that in these cases the reactor was partly filled with feed stock. Since this contributed to carbon deposition on the catalyst, it must be assumed that under normal conditions a longer lifetime of the catalyst could be expected.

Regeneration of the catalyst was carried out by burning off the carbon from the catalyst in the reactor using a current of nitrogen with an addition of 1 - 2% oxygen. Regeneration was difficult in this experimental run since no preheater for the nitrogen was available and the regeneration temperature required was obtained by raising the temperature in the reactor.

After completion of the regeneration, the reactor was operated on product again with a space velocity of 0.625 volumes of liquid feed per volume of catalyst per hour. The operating temperature was 725 - 797°F. and the conversion was about 50%. During this operating period the reactor twice reached excessive temperatures - once the temperature rose in a very short time to 1,148°F. and the second time the temperature reached 1,560°F. In both cases the injection of liquid feed was stopped immediately and cold gas was circulated through the reactor; in spite of these measures the temperature could not be controlled. The reactor had to be shut down for a short period to install a new thermocouple. When operations were resumed the space velocity was about 1 : 1 but the conversion amounted only to 40%. It was attempted to increase conversion by reduction of the space velocity to approximately 1 : 0.6 and by increase of the reactor temperature to 860°F., but this was without success. The conversion continued to vary between 30 and 40%. The reactor was subsequently shut down to change the catalyst.

The data obtained in these experimental runs are not conclusive since the product fractionator did not operate satisfactorily and the material recycled to the reactor contained, at times, up to 20% of material boiling below 329°F., thereby making it appear as if the conversion were greater than it actually was.

Distillation.

The hydroformer bottoms which were to be reformed by means of the Arobin process were distilled under vacuum (3 mm. Hg.) in order to obtain a product which is free from the highest boiling material which would lead to premature coking of the catalyst. For a distillate with an end point of 572 - 590°F. the yield of bottoms was 10%, whereas for a distillate with an end point of 590 - 608°F., the yield of bottoms was reduced to 7%. The bottoms were used as pasting oil in the high-pressure coal hydrogenation.

The product from the Arobin unit was stabilised in a column operating at a pressure of 45 - 59 psig., giving a product with a vapor pressure of 4.4 - 5.9 pounds Reid. The yield of C_2 to C_4 hydrocarbons obtained by stabilisation was 13 - 14%, based on the distilled hydroformer residue charged to the process. The composition of the low boiling material is given in the following table which also compares the data from laboratory runs with actual plant operations:

Table 1

	Lab. Experiments	Plant Runs
CH_4	2% by wt.	1% by wt.
C_2H_6	14% " "	12% " "
C_3H_8	36.2% " "	35% " "
iso C_4H_{10}	29.4% " "	32% " "
n-C_4H_{10}	18.4% " "	20% " "

The small amounts of tail gas which are released when the high-pressure unit is depressured are not considered. The C_5 content in the stabilizer reflux could be kept at about 2% so that the bulk of the pentane remains in the Arobin product.

In the product column the stabilized product was separated into the finished product with an end point of 329°F. and the recycle stock which constitutes the bottoms. The aromatic content of the product amounts to 65 - 70% by volume. The production during the entire operating period was 5,440 barrels of Arobin. The yield was 73%, based on the hydroformer bottoms processed. The losses were composed of 14% cracking gases, 8% bottoms from the primary distillation and 5% losses by leakage. The most important data on the quality of the product are given in the following table which again gives a comparison between the data obtained on laboratory and plant products. The data on the plant product give results obtained over a 4-month period during which a total of 3,890 barrels were produced.

Table 2

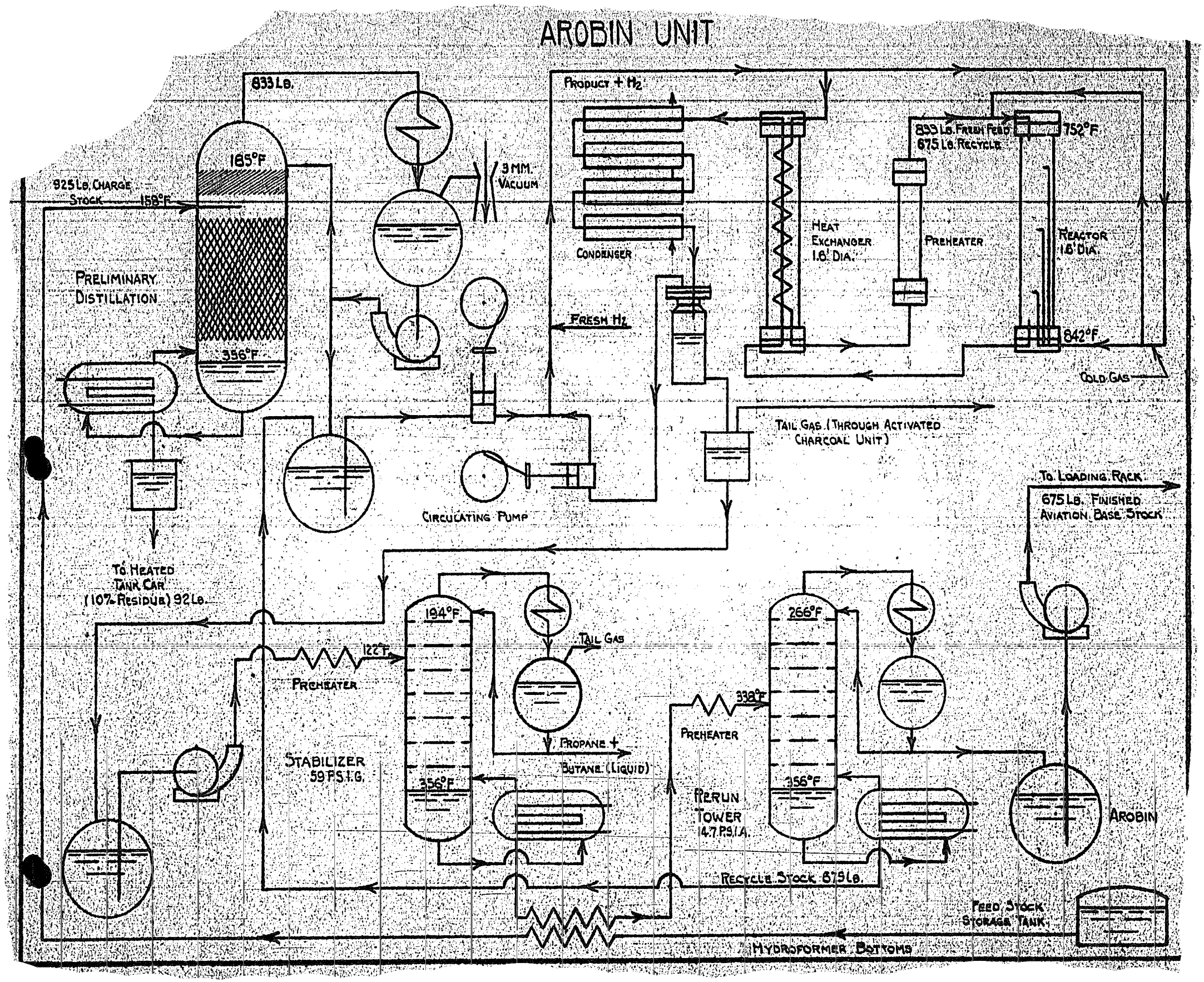
	Lab. Experiments	Plant Runs
Density $\frac{20°C}{4°C}$	0.807	0.805 - 0.814
API gravity	43.0	41.5 - 43.4
Reid vapor pressure	5.9	4.4 - 5.9
Aromatics % by vol.	65	65 - 69
Octane no.	86	86 - 87.5
Octane no., leaded	93.5	91.5 - 93.5
IBP	117°F.	113 - 131°F.
To 212°F.	20%	16 - 20%
To 248°F.	41%	-
To 257°F.	-	37 - 45%
EP	333°F. (99%)	331 - 342

The following tentative specifications have been proposed to the German Air Ministry on the basis of the properties of the product produced so far. The specifications are given in the following table:

Table 3

Density $\frac{20^{\circ}C}{4^{\circ}C}$	0.795 - 0.825
API gravity	39.3 - 45.6
Iodine No.	4 max.
Corrosion at 122°F.	negative
Freezing Point	-76°F. max.
Reid vapor pressure	7.4 max.
Octane no.	82 min.
Octane no. + 4.5 cc. TEL/gal.	90 min.
Aromatics	60 - 70% by vol.
Distillation	
IBP	104°F. min.
10%	176 - 203°F.
30%	221 - 248°F.
50%	257 - 284°F.
90%	311 - 329°F.
E. P.	347°F. max.
Loss	2% max.
Reaction of residue	neutral

AROBIN UNIT


833 Lb.
185°F
925 Lb. Charge Stock
158°F
3 MM. Vacuum
Product + H2
Condenser
833 Lb. Fresh Feed
675 Lb. Recycle
752°F
Heat Exchanger 1.6' Dia.
Preheater
Reactor 1.6' Dia.
Preliminary Distillation
Fresh H2
356°F
842°F
Cold Gas
Tail Gas (Through Activated Charcoal Unit)
To Loading Rack
675 Lb. Finished Aviation Base Stock
Circulating Pump
To Heated Tank Car (10% Residue) 92 Lb.
194°F
122°F
Preheater
Tail Gas
266°F
339°F
Preheater
Propane + Butane (Liquid)
Stabilizer 59 P.S.I.G.
356°F
Rerun Tower 14.7 P.S.I.A.
356°F
Arobin
Recycle Stock 675 Lb.
Feed Stock Storage Tank
Hydroformer Bottoms