U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-266

High Pressure Experiments
Lu 1.

6/30/44

From Dr. Pier's Private Files.

A MODULUS FOR THE COAL ASH.

Summary

Mineralogic investigations and analysis of coal ash are used to express a modulus for the characterization of coal ash.

According to Simek 1/ mineralogical studies of the coal ash have led to the following conclusions:

1). All MgO is present as the biotite, $K_2O.4MgO.2Al_2O_3.6SiO_2.H_2O$

2). Potassium not combined in biotite is present as the muscovite, $K_2O.Al_2O_3.6SiO_2.2H_2O$.

3). Sodium is combined to $Na_2O.Al_2O_3.6SiO_2$.

4). Phosphoric acid exists as $AlPO_4$.

5). Lime, other than $CaSO_4$, $CaCO_3$ or organically bound lime, is present as anortite, $CaO.Al_2O_3.2SiO_2$.

6). The balance of Al_2O_3 and SiO_2 exists as $Al_2O_3.2SiO_2.2H_2O$.

These assumptions are applicable to water insoluble carbonate ash. No statements are made regarding the iron found in the coal ash, it being evidently assumed to exist as the oxide or pyrite. It is further assumed, that at the ashing temperature (700 - 800°) silicates suffer no other changes than the loss of water of hydration. The hypothesis therefore remains applicable to low or intermediate temperature coking.

Attempts are here made to evaluate the ash analyses in the light of the above assumptions, and to calculate some kind of factor for the characterization of the ash. As a result, this modulus will indicate this excess or deficiency of Al_2O_3 - SiO_2

1/ Gluckauf, 80-th year, issue 3/4, Jan. 22, 1944, pp. 33 - 37.

after the combination with the alkalies or alkaline earth constituents.

In the usual methods of ash analyses, the SO_3 and CO_2 present in the coal, the sodium in the ash and the water insoluble carbonate ash are not determined, and only approximate values could be obtained.

The residue after ignition was assumed to equal the water insoluble carbonate ash, the CO_2 and SO_3 needed as the acidic constituents demanded for the neutralization of CaO were left out of consideration. Nor has the TiO_2 contents of the ash been taken into account.

Calculation of the Modulus.

1 MgO in biotite ($K_2O.4MgO.2Al_2O_3.6SiO_2.H_2O$) represents:

$$1/4\ K_2O:\quad 1/4 \times \frac{94.20}{40.32}\ K_2O = 0.58\ K_2O$$

$$1/2\ Al_2O_3:\quad 1/2 \times \frac{101.94}{40.32}\ Al_2O_3 = 1.26\ Al_2O_3$$

$$3/2\ SiO_2:\quad 3/2 \times \frac{60.06}{40/32}\ SiO_2 = 2.24\ SiO_2$$

1 K_2O in muscovite represents 1 Al_2O_3: $\frac{101.94}{94.20}\ Al_2O_3 = 1.08\ Al_2O_3$

muxcovite represents 6 SiO_2: $\frac{6 \times 60.06}{94.20}\ SiO_2 = 3.82\ SiO_2$

In $AlPO_4$, 1 P_2O_5 represents 1 Al_2O_3: $\frac{101.94}{142.04}\ Al_2O_3 = 0.72\ Al_2O_3$

1 CaO in anortite represents 1 Al_2O_3: $\frac{101.94}{55.08}\ Al_2O_3 = 1.82\ Al_2O_3$

CaO in anortite represents 2 SiO_2: $\frac{2 \times 60.06}{56.08}\ SiO_2 = 2.14\ SiO_2$

$$M = Al_2O_3 - 1.26\ MgO - 1.08\ (K_2O + Na_2O - 0.58\ MgO) - 0.72\ P_2O_5 -$$
$$-1.82\ CaO + SiO_2 - 2.24\ MgO - 3.82\ (K_2O + Na_2O - 0.58\ MgO) -$$
$$- 2.14\ CaO$$

Formula for the Modulus: $M = Al_2O_3 + SiO_2 - 0.65\ MgO - 4.90\ (K_2O + Na_2O) - 3.96\ CaO - 0.72\ P_2O_5$

Only relative values of this modulus are provisionally used to predict similar information about the nature of coal ash as from the alkalinity determined by us by the conventional methods.

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-267

High Pressure Experiments
Lu 558

November 15, 1941

ISOMERIC AROMATIC HYDROCARBONS.

From Dr. M. Pier's Private Files.

The following compilation contains the aromatic hydrocarbons from C_6 to C_{10}, arranged by the nature of the side chains with increasing number of C atoms. The boiling points, specific gravities, heats of combustion, the mixture octane number 1/ and the occurrence in gasolines is also given for them. All the hydrocarbons given in the table have been prepared industrially, but occur occasionally as mixtures, which can not be separated by fractionating.

Signed -- Eenkel

W. M. Sternberg

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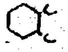
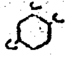
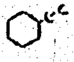
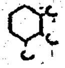
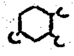
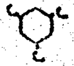
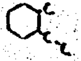
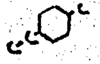
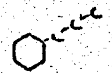
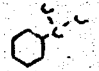
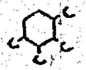
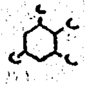
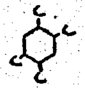
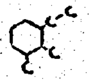
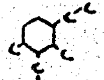
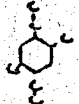
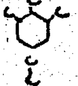
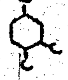
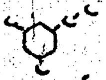
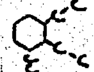
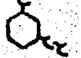
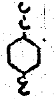
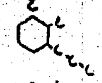
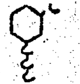
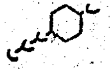
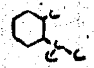
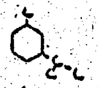
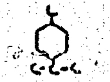
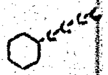
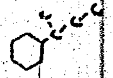
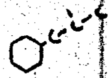
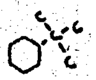
1/Calculated from aniline equivalents by Lovell, Campbell and Boyd, Ind. Eng. Chem., vol 23, p.26. The determinations were made in about 20% solutions by volume of the corresponding hydrocarbons in a gasoline with the octane number of 55.

Hydrocarbon		Structural Formula	Boiling Point, °C	Specific Gravity d_4^{20}	Heat of Combustion kcal/mol	Octane Number of Mixture Motor	Octane Number of Mixture Research	Presence in Gasoline Proven	Techn. Production
C_6H_6,	Benzol		80.1	0.8737	782.00	(87)	(109)	+	+
C_7H_8,	Toluol		110.6	0.8670	934.2	(90)	(120)	+	+
C_8H_{10},	o-xylol		144.0	0.8801	1090.9	(97)	(121)	+	+
	m-xylol		137.0	0.866	1090.9	(104)	(144)	+	
	p-xylol		138.4	0.8610	1087.1	(104)	(154)	+	
	ethyl benzol		136.15	0.8667	1089.0	(97)	(128)	+	+
C_9H_{12}	1,2,3 tri-methyl benzol (hemimellitine)		176.1	0.8951	—	—	—	+	+
	1,2,4 tri-methyl benzene (Pseudocumol)		169.2	0.8762	1239.8	—	(123)	+	
	1,3,5 tri-methyl benzene (mesitylene)		164.6	0.8653	1242.8	(109)	(161)	+	
	1 methyl, 2 ethyl benzene		164.9	0.881	—	—	(107)	+	+
	1 methyl 3 ethyl benzene		161.5	0.8690	1243.2	—	(130)		
	1 methyl 4 ethyl benzene		161.2	0.866	—	—	(147)		

Hydrocarbon		Structural Formula	Boil. Point °C	Spec. Grav. d^{20}_4	Heat of Combust.	Octane number of mixture motor	Octane number of mixture research	Presence in Gasoline Proven	Technical Production
C_9H_{12},	n propyl benzene		158.6	0.8628	1245.7	-	(137)	+	+
	i-propyl benzene		152.4	0.8581	1246.5	(87)	(128)		+
$C_{10}H_{14}$,	1,2,3,4 etetramethyl benzene (prehnitene)		204.5	0.901	1389.8	-	-	+	+
	1,2,3,5 tetra methyl benzene (isodurene)		198.0	0.8906	1389.8	-	-	+	
	1,2,4,5 tetra methyl benzene (durene)		196.0	0.8380	1388.3	-	-	+	
	1 ethyl, 2,3 dimethylbenzene		189.0	0.8704	-	-	-	-	+
	1 ethyl 2,4, dimethyl benzene		184.0	0.878	-	-	-	-	
	1 ethyl 2,5 dimethyl benzene		185.5	0.8750	-	-	-	-	
	1 ethyl 2,6 dimethyl benzene		155.5	0.8740	-	-	-	-	
	1 ethyl 3,4 dimethyl benzene		189.0	0.8704	-	-	-	-	
	1 ethyl, 3,5 dimethyl benzene		185.0	0.861	-	-	-	-	
	1,2 diethyl benzene		184.0	0.8662	-	-	-	+	+
	1,3 diethyl benzene		180.5	0.8597	-	(126)	(145)	+	

Hydrocarbon		Structural Formula	Boil. Point °C	Specif. Grav. d_4^{20}	Heat of Combust.	Octane number of mixture motor	research	Presence in Gasoline Proven	Technical Product.
$C_{10}H_{14}$	1,4 diethyl benzene		183.0	0.865	-	-	(158)	-	
	1 methyl, 2 n-propyl benzene		184.0	0.8740	-	-	(114)	-	+
	1 methyl 3 n-propyl benzene		181.5	0.8620	1405.5	-	(130)	-	
	1 methyl 4-n propyl benzene		182.5	0.861	-	-	(130)	-	
	1 methyl 2-iso-propyl benzene		175.5	0.876	1402.9	-	(117)	-	+
	1 methyl 3 iso-propyl benzene		175.7	0.8606	1409.5	-	(134)	-	
	1 methyl 4 iso-propyl benzene (cymene)		177.3	0.8570	1402.8	-	(136)	-	
	n butyl benzene		182.6	0.8658	1401.9	(82)	(115	+	+
	a methyl n propyl benzene (isobutyl benzene)		170.0	0.8528	-	-	(115)		+
	b methyl n propyl benzene (sec. butyl benzene)		171.0	0.8577	-	(76)	(119)		
	α, α dimethyl ethyl benzene (tert. butyl benzene)		167.0	0.8623	1400.4	(88)	(130)		

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

THREE PAPERS ON PREVENTION OF EXPLOSIONS IN AIR SEPARATION INSTALLATIONS

From Dr. M. Pier's private files.

I.

Leuna, Jan. 1943
Scholven

CONTENTS:

I. The Importance of Hydrocarbons in the Operation of the Air Separation Equipment.

According to experience, acetylene and other hydrocarbons are always present in the air, and especially in the neighborhood of large industrial installations, and are drawn into the intakes of the air separation units. The boiling points of these compounds are above those of oxygen and nitrogen. They therefore become enriched in liquid oxygen during the liquefaction and separation of air. The hydrocarbons dissolved in liquid air present a danger, because, when the limits of their solubility are exceeded, they occasionally separate in the solid form, producing explosion centers.

When the hydrocarbon content is mentioned below, the total hydrocarbon content, including the acetylene is meant. In most cases, acetylene is present in far smaller amounts than the other hydrocarbons. However, because of its tripple bond, acetylene is by far the most unstable hydrocarbon, is very reactive, and must be considered an explosive of high destructive power, when in the solid form in the presence of oxygen. Even small amounts of acetylene depositions may be the cause of very violent explosions. Other hydrocarbons may be considered less dangerous, and are only dangerous in larger amounts.

It is therefore a basic requirement for safe operations of an air separation installation, that the air be as free from hydrocarbons, as possible. There exist no practical methods to remove the hydrocarbons present in the air, and the purest air available must be drawn into the system. For that purpose, the air intakes must be arranged from different directions, to draw air in at any wind directions, which produce air freest from used air and off-gases.

Occasionally, hydrocarbons in the air to be decomposed may come from the compressors in which the air is compressed to pressures required for its separation. In piston compressors, the oil used in the lubrication of the pistons may become decomposed at high temperatures of the cylinder walls, producing acetylene and other hydrocarbons. This danger is avoided in the use of turbocompressors.

To avoid a dangerous concentration of acetylene and other hydrocarbons in the air in spite of all precautions, various improvements have been introduced into the air separation equipment. In addition, precautions have been introduced in the operations, which will be discussed below.

II. Safety Measures Against the Enrichment in Hydrocarbons.

A. Constructional Precautions.

The two-column air separation apparatus using the Linde process uses a heat exchanger between the two columns, which acts as a liquefier of nitrogen in the pre-separation column and simultaneously as an evaporator for oxygen in the upper column. This, so-called main condenser, is a bundle of vertically arranged small tubes, in which the nitrogen of the preseparation column is condensed, while the oxygen outside the columns is present in the boiling state. The hydrocarbons entering the unit with the air to be decomposed become enriched in the liquid oxygen bath, in accordance with their vapor pressures.

The hydrocarbon enrichment in this part of the apparatus is particularly dangerous because of the large amounts of liquid oxygen present. Efforts have therefore been made to avoid the accumulation of hydrocarbons resulting from the evaporation of oxygen, and to withdraw the oxygen in the liquid state. In addition, the danger of separation of solid hydrocarbons,, in particular the formation of acetylene asters, is greatest at the still edges of the liquid bath, where the evaporating oxygen does not circulate, while the liquid oxygen in all parts of the bottom of the condenser is kept in vigorous agitation.

The original flat bottom of the principal condenser has for that reason been later given a funnel shape. The liquid oxygen is withdrawn at the lowest part in the center of the bottom. At first, only part of the liquid oxygen was withdrawn there to be evaporated in a separate additional condenser, later all the oxygen produced. (cf fig. 1)

In addition, several "bungholes" were provided in the outer mantel of the main condenser, and withdrawing some of the liquid oxygen through them also results in an improved circulation of the liquid.

These changes have not eliminated the danger of hydrocarbon enrichment, but transferred it away from the main condenser, where the largest amounts of liquid oxygen are accumulated. In the main condenser a body of liquid oxygen is evaporated, while in the auxiliary condenser the oxygen is inside the tubes, while nitrogen condenses in the space outside the tubes. Oxygen enters the tubes in the liquid state and is evaporated as it passes the bundle of tubes. In order to prevent the formation of a zone in the bottom part of the tubes, where solid hydrocarbons would form towards the end, the auxiliary condenser is so operated, that a small part of the oxygen fails to evaporate, and remains liquid. This liquid continuously rinses the tubes. The liquid oxygen is separated from the gas in a catchpot and vented fromttime to time. This catchpot is called the "acetylene separator", because most of the acetylene (as well as the other hydrocarbons) remains in the liquid oxygen and is separated with the oxygen.

The parts of the auxiliary condenser and the acetylene separator, where there is an accumulation of acetylene and hydrocarbons may be warmed up at stated time intervals, evaporating the residues which may have accumulated in spite of the rinsing. There is no need of thawing out the whole air separation installation during this warming up of the auxiliary condenser and the acetylene separator. Modern equipment is so operated, that while the auxiliary condenser is being warmed up, the main part may still continue in operation, by withdrawing the gaseous oxygen from the main separator. During the short time of partial thawing out (a few hours are usually sufficient for the purpose), the unit is operated in the way flat bottom condensers were operated, with a withdrawal of gaseous oxygen. This arrangement has been found particularly successful in the Linde-Fränkl installations.

B. Operational Precautions Against the Hydrocarbon Accumulation.

In addition to the above constructional improvements, the following operational precautions have been introduced, and they have been found adequate:

1) The selection and control of air intakes,
2) The analytical supervision of the equipment,
3) The draining off of liquid oxygen, and
4) The maintenance of regular thawing out periods.

1). The wind directions and wind velocity are regularly watched to permit the selection of the most favorable air intake conditions. This is done by means of wind direction indicators and anomometers installed in several locations at a high level . Anemographs tell the direction of the wind in the two air inlets. Care is taken always to use air from the most favorable air inlet. In fog, or in still weather precautions against the rise of the hydrocarbon level are immediately put in operation (increased draining of the liquid, v. infra).

The causes of increase in the hydrocarbon level during normal operations must be immediately discovered, and whenever possible eliminated. Cases have, e.g., occured when the increased acetylene enrichment was caused by a puffing locomotive or to a smoking potato-greens fire.

2). Regular determinations of acetylene and total carbon are made in the liquid oxygen of the main condenser. For this purpose, samples are withdrawn hourly from the installation for the determination of acetylene, and every two hours for the determination of carbon.

The contents of acetylene and hydrocarbons in liquid oxygen are usually expressed in mg/5 li. liquid oxygen. As a rule, the carbon content is many times greater than the amount of carbon in the acetylene present (e.g., in our Linde-Fränkl process it normally is 300 - 400 times larger).

Under normal air conditions, determinations from our Linde-Fränkl equipment indicate the presence of 0.1 - 0.2 mg acetylene and 50 - 60 mg carbon in 5 liters of liquid oxygen. When starting a unit and during the thawing out of the auxiliary condenser, i.e. under operating conditions, during which no liquid oxygen is removed, there is normally an increase in these amounts, which disappears of itself in a short time.

Continuous determinations were made in installations in which no enrichment was observed beyond 0.5 mg acetylene and

150 mg total carbon/5 li. liquid oxygen. The maximum permissible amount in acetylene and carbon can not be stated with any assurance. Whenever an acetylene content of 1 mg or a carbon content of 200 mg/5 li. is observed during normal operation of the unit, the management is immediately notified.

A decision on the continuation of operations or an immediate shut-down can only be reached with an exact knowledge of conditions. If, e.g., it is considered permissible to start the unit again after the elimination of the difficulties, and the air again indicates the presence of 0.5 mg acetylene or 200 mg total carbon/5 li. liquid oxygen, the continuation of forcing contaminated air into the unit becomes uncertain. No universally acceptable limits can therefore be given.

2. To permit one to counteract the enrichment with acetylene and hydrocarbons, part of the liquid oxygen is continuously drained from the acetylene separator and from the different sampling connections of the main condenser.

To do this, the evaporation of liquid oxygen in the auxiliary condenser is so conducted, that a small part of the oxygen from the adjoining acetylene separator is collected in the liquid form. This separator is emptied every two hours down to a small residue of the liquid.

Residues from the evaporating oxygen, which might be kept fastened to the small tubes of the auxiliary condenser, will thus be rinsed off and let down with the liquid. The determination of acetylene in the liquid oxygen in the acetylene separator actually shows a progressive increase in the acetylene content, which is some 50 times greater than in the values found for the main compressor. To a certain extent, the rinsing of the condenser tubes accomplishes its purpose.

When samples are withdrawn for the determination of acetylene and of carbon, the actual sampling is done after flushing the outlets each time with 5 to 10 liters of liquid oxygen. In this way, hydrocarbons which may eventually have deposited after the steaming out the pipe line will not cause the analytical results to be in error.

In addition, liquid oxygen is withdrawn under normal operating conditions from three taps uniformly distributed in the outer wall of the principal condenser above the funnel shaped bottom. 5 liters are drained through three 25 mm i.d. connections at the highest possible rate every 8 hours to prevent any stagnation of the oxygen which is to be evaporated at the bottom of the main condenser.

Whenever the acetylene or total carbon contents rise, or in the absence of wind, or in foggy weather, or in general with a weather which according to experience invariably leads to raising the acetylene and hydrocarbon level in the air separation equipment, the amount of liquid withdrawn from the acetylene separator is immediately doubled or trebbled. The amounts of liquid withdrawn from the taps is similarly increased.

A lowered acetylene and hydrocarbon concentration in the liquid oxygen can result from an increased amount of condensation of the liquid, produced by increasing the amount of the liquid oxygen drawn off from the main condenser. This may be done through the connection for the normal withdrawal of the liquids for sampling; or else, through a connection on the same pipe line intended for "rapid evacuation", a large amount of oxygen is pressure-released and led into the evaporator adjoining the oxygen pipe line. This connection permits an instantaneous withdrawal of several 100 liters of liquid oxygen.

4. According to experience, in spite of all these precautions continuously used in operation, a certain accumulation of acetylene and hydrocarbon residues can not be avoided in the different parts of the unit, especially inside the auxiliary condenser tubes. For these reasons, the auxiliary condenser is warmed up or the whole unit is thawed out after a definite period of operation. In the auxiliary condensers the time interval between two successive thawings-out is 40 days, while the interval between the thawing-out of the main apparatus by a total shut-down is 200 - 250 days.

III. Success of the Precautionary Measures.

Four explosions have occurred between 1927 and 1933 in our air separation installation, which at that time consisted of the older Linde units with counter current heat exchangers. All the explosions happened in apparatus in which the total oxygen was evaporated in the main condensers with flat bottoms, with no appreciable amount of oxygen withdrawals in the liquid state. They were the reason for the introduction of the above described constructional changes and operational safety measures.

As a result, no explosions have happened since 1933. The installation mentioned, with the changes introduced, was still in operation up to 1938. In addition, since 1933 a new installation on the Linde-Fränkl principle has been in trouble free operation. In this, the air is cooled in reversible heat exchangers, and the experience with the old Linde installation was freely used in the safety features of its construction.

Auxiliary condensers were added to the old installation during their reconstruction, which permit the withdrawal of about one third of the oxygen in the liquid form from the main condensers. The new Linde-Fränkl installations are provided for the withdrawal of all the liquid oxygen with a subsequent evaporation in the auxiliary condensers. The success of these measures is seen in the lowering of the average acetylene and hydrocarbon contents.

In the old equipment, the average acetylene content of the oxygen was 0.3 - 0.5 mg acetylene and 100 mg total carbon, while the hydrocarbon level of the new Linde-Fränkl units is 0.1 - 0.2 mg acetylene and 50 - 60 mg carbon in 5 liters of liquid oxygen.

Signature undecipherable

W.M. Sternberg,
March 14, 1947.

II.

Questionaire sent to Scholven, Gelsenberg, Pölitz, Welheim, Brabag, Theinraun, Lutzkendorff, Blechhammer, Brüx.

High Pressure Experiments
P/Lu 558 March 9, 1943.

Questionaire
Precautions against Explosions in Air Separation Installations.

An exchange of experiences on safety measures against explosions in air separation installations is advisable for the sake of industrial safety. You will accordingly find in the appendix a summary of safety measures introduced in Leuna air separation installation for the prevention of acetylene and hydrocarbon explosions, and we request you to reply to the following questions:

1) Are your air separation installations equipped with any additional condensers in the liquid state?

If so, a) What proportion of the total oxygen production is withdrawn from the main condenser?

b) Is the auxiliary condenser operated in a way to have some of the liquid oxygen (what proportion?) collect in the acetylene separator?

Or, finally, is the auxiliary separator operated dry, and from time to time rinsed with liquid by increasing the pressure?

2) Do you have quantitative determinations made for acetylene and hydrocarbons at your air separation plant?

If so, what is the acetylene and total carbon content in the liquid oxygen of your main condensers, and in the acetylene separator.

a) Under normal operating conditions?

b) At occasional enrichment?

3) Do you determine occasionally or regularly the acetylene or total carbon content in the intake air or in the gaseous oxygen boiling off from the separation unit:

If you do, what are the values obtained, and what are the values in samples withdrawn simultaneously from the main condenser and the separation unit?

4) Do you have special air intake pipe lines?

If you do, is air forced through the pipe line, by positive pressure, or sucked in through it under reduced pressure?

5) What is the average period of operation of your separation units and of the auxiliary separators, if any, and of the acetylene separators before thawing-out?

6) Have you had any explosions in the air separation installations?

If, so a) in what parts of the installations?
b) could the causes of the explosions be definitely established?

7) Have you observed in your air separation equipments any accumulation of oxides of nitrogen?

If so, a) in what parts of the apparatus have such accumulations been observed?
b) what oxides of nitrogen have been identified?

In conclusion, we wish for an opinion to what extent the precautions introduced in Leuna have contributed to the prevention of explosions, and what additional safety measures should be introduced?

I.G. Farbenindustrie Aktiengesellschaft,

Two illegible signatures.

WINTERSHALL AKTIENGESELLSCHAFT

Lützkendorf Works, Krumpa near Merseburg.

3/9/43 (?)

Discussion of Safety Measures for the Protection Against Explosions in Air Separation Installations.

We reply to your questions as follows:

1). Our air separation installations are equipped with auxiliary condensers. Almost all of the liquid oxygen is removed from the main condensers in the liquid state and evaporated in the auxiliary condensers. The gas from the main condenser is used to regulate the peaks. With a poorly operating auxiliary condenser, this amount may reach 30 - 40% of the total gas. The liquid is either continuously drawn into the acetylene separator and evaporated in an evaporator for the purpose (10 - 25 nm^3/hr), or else some 40 liters are daily drained from the separator and discarded.

2). Normally, only qualitative determinations of acetylene are made, following Linde's directions, with ammoniacal silver nitrate; we get there a slight deposit, black because of the silver sulfide. We have made a quantitative determination as a result of your inquiry, and found that the amount of acetylene + H_2S in 10 liters of liquid oxygen was 1.04 mg, of which H_2S was only present in traces, while the amount of hydrocarbons was 52.0 mls, with the C value of 3.7.

3). Air is taken in through 2 parallel pipe lines about 800 m in length, from the south side.

4). No analyses were made of the intake air.

5). The installation operates 3 - 6 months; the auxiliary condensers and the acetylene separators are thawed-out after disconnecting from the condenser after about 2 - 3 months of operation.

6). We have had no explosions.

7). No oxides of nitrogen have been observed.

We have observed during the thawing out of the auxiliary condenser an enrichment in hydrogen sulfide(by the strong odor). It may be doubtful whether the periodic thawing-out of the auxiliary condenser before any loss in its efficiency is necessary. We consider other precautions being too far fetched for Lutzkendorf.

We hope to have been of service to you with our information.

Wintershall Aktiengesellschaft
Lützkendorf Works

CHANGES IN THE MAIN CONDENSER

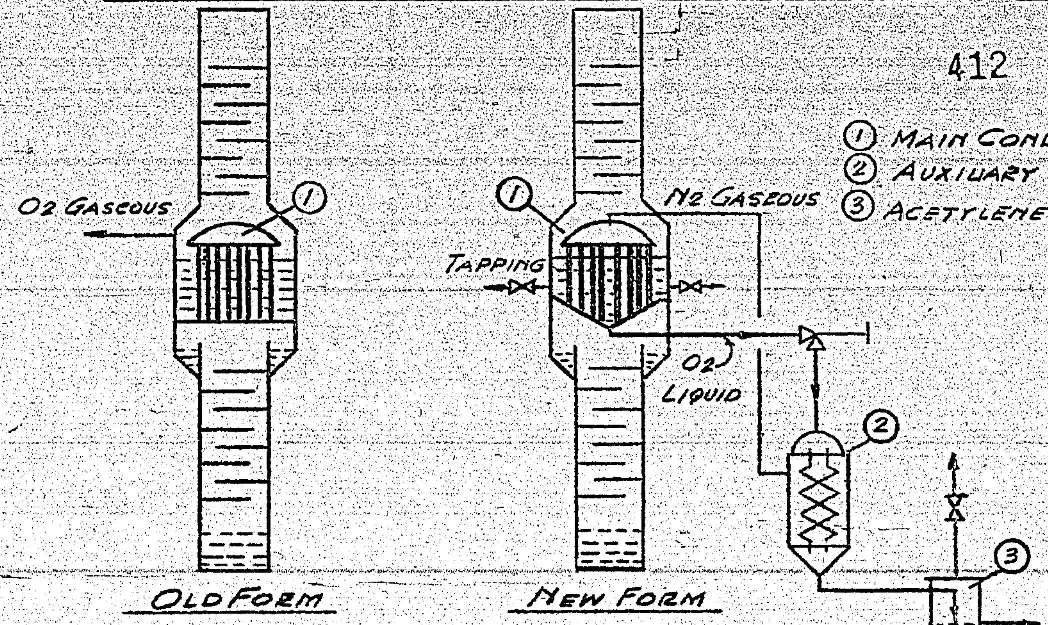


FIG. 1
PLACES FOR WITHDRAWAL OF LIQUID OXYGEN FROM THE LINDE-FRANKI UNITS

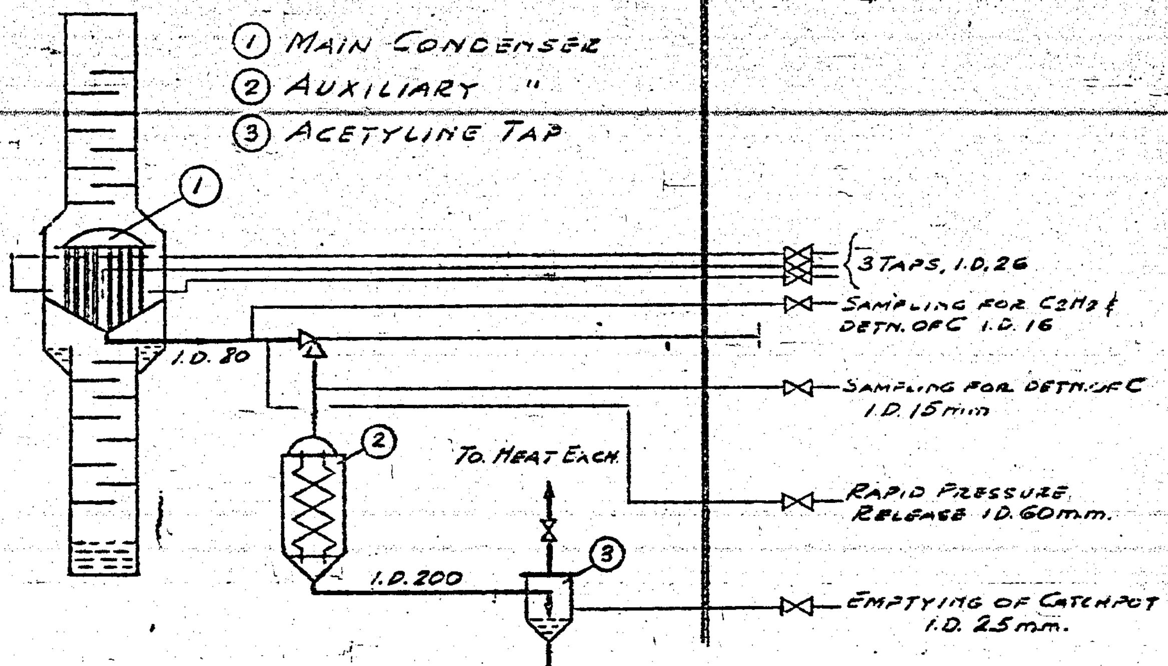


FIG. 2

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HYDROGENATION OF LETDOWN

By V. Simon, 13. Feb, 1942

Letter addressed to Scholven, Gelsenkirchen-Buer.

At the request of your Dr. Urban we made some continuous small scale experiments to reduce the asphalt content (Asphaltspiegel) of your 300 atm letdown @ 600 atm H_2 pressure.

The letdown was hydrogenated alone in a straight run with a thruput of 0.7 kg/lit./h @ 25 mV (476°C) with 1% Grude-iron catalyst. Both asphalts and pure coal were still further decomposed more than 50%. At the same time the quantity of heavy oil was reduced very little and the asphalt content in the heavy oil dropped from 18.8 to abt. 8%. The yield of new products to 325°C was barely 0.2 and gasification was 25% of new formation + gasification. At 24 mV (460°C) the asphalt was decomposed almost as much, to 8.5% of the heavy oil, and the middle oil yield was only abt. 0.1.

By recycling the centrifuge oil topped at 325°C, without L.T.C. of the centrifuge residue, and a fresh feed thruput of 0.3 under otherwise equal conditions as above, the asphalts were completely decomposed, while pure coal decomposition, new formation -325°C and gasification were about the same as with a straight run. The asphalt "Spiegel" in the heavy oil was about 10%. The quantity of liquid phase gasoline, at about 10% of gasoline + middle oil, was less than with Scholven liquid phase catchpot product. The gasoline was richer in aromatics than Scholven liq. ph. gasoline, including light ends 45%/Wt. aromatics. The middle oil, with only 1.6% phenols and aniline point -43, was appreciably poorer in phenols and H_2 than Scholven liquefaction middle oil. The catchpot heavy oil (recycled), obtained at a relatively low catchpot temperature (21 mV = 408°C), furnishes a good fuel oil with relatively low viscosity.

With both operating methods the quantity of letdown to be processed was reduced to little more than half of the original letdown (at equal solids content) by the 600 atm processing, because roughly 50% of the organic solids present are further decomposed.

To avoid trouble in preheating, the letdown had to be thinned by recycling or the addition of pasting oil. When hydrogenating this letdown together with considerable quantities of coal and 600 atm pasting oil no difficulties need, therefore, be expected.

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H_2-CONTENT OF HYDROGENATION OILS

Ludwigshafen, 24. Feb. 1942.

The Scholven table of H_2-values was supplemented by Lu with values of 700 atm experiments. All 700 atm oils contain roughly 1-2% more H_2, while in L.T.C. the H_2-content deteriorates sharply in both cases. These H_2-poor L.T.C. oils might, in certain cases, best be added to the fuel oil. (See table below).

C-H Analyses of Various Products from Stall 804 at Ludwigshafen run with Upper Silesian coal to Gasoline and Middle Oil, August 1941.

	% C	% H	gH/100 gC
Letdown (free of solids)	89.83	7.01	7.80
Catchpot heavy oil	89.57	8.12	9.07
Centrifuge oil (free of solids)	90.45	7.45	8.24
Centrifuge residue oil (free of solids)	90.46	7.42	8.20
L.T.C. oil	90.25	5.86	6.49
Pasting oil (free of solids)	91.05	7.36	8.08
Catchpot middle oil	87.06	9.68	11.14

Arranged in Order of Rising gH/100 gC

L.T.C. Oil,	6.49
Letdown	7.80
Pasting Oil	8.08
Centrifuge Residue Oil,	8.20
Centrifuge Oil,	8.24
Catchpot Heavy Oil	9.07
Catchpot Middle Oil	11.14

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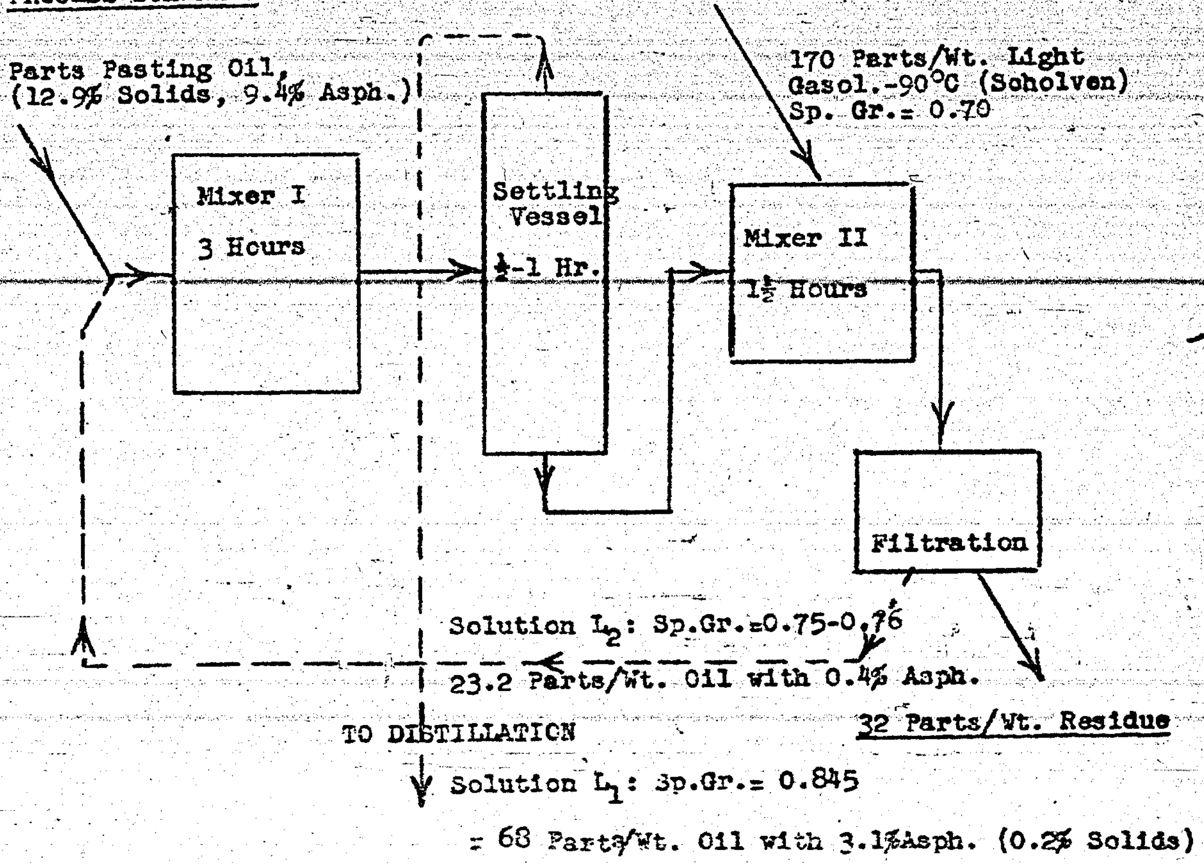
FILTRATION OF LETDOWN

By Löcker, Ludwigshafen, 27 Jan. 1941.
(See also T-177 and T-206)

I. Removing the Solids and Asphalt from Pasting Oil by Adding 170 Parts/Wt. of Light Gasoline.

Bituminous coal pasting oil from Converter 411, with 12.9% solids, 32.3% ash in solids, 9.4% asphalt in oil, spec. grav= 1.06/100°C, was processed for a period of 4 days in 4 experiments, according to the following arrangement.

PROCESS SCHEME I



Filter Yield, small scale, abt. 1500 kg. pasting oil/m^2/h.

Gasoline Losses in Filter Residue:

By suction and ventilation at room temperature the filter cake was completely freed of gasoline in an hour, i.e. the gasoline losses can be kept very low in plant operations. (Circulating air through the cake at up to 45°C, adsorption of the small quantities of gasoline by A-coal).

Analyses of oils recovered:

Sp. Gravity = 1.065/20°C
Viscosity/50°C= 7.3°C
Coke test, 7.5
The oil can be used as mixture component to fuel oil.

Utilization of the gasoline-free residue:

(L.T.C. analyses of the residue yielded 53% coke, 25.9% tar = 8.3% of pasting oil)

Extraction of the asphalt (stirred with benzol 3 times, filtered)

Extracted by benzol: 15.1 g oil (0.4 g solids/100 g pasting oil or 40 g total residue), of which 27.7% asph. & 0.2% ash. (high ash due to poor filtration).

II. Removing Asphalt and Solids from Pasting Oil by Heavy and Light Gasolines.

The process is similar to Scheme I, except that the stock is first precipitated with 200 parts/wt. of gasoline 90-180°C (dehydrogenation fraction of the Brabag prehydrogenation gasoline) and the oil solution containing gasoline so obtained was drawn off after decantation and then further processed with light gasoline according to Scheme I.

A very small test was run:

Input: 25 g pasting oil, 50 g gasol. 90-180°C,
60 g light gasoline-90°C.

Output: L_1, 5.8 g oil @ 3.4% asphalt,
L_2, 10.1 g " @ 2.2% asphalt,

Total 15.9 g oil @ 2.8% asphalt,
9.0 g dry residue,

Total 24.9 g

The dry residue extracted with benzol produced:

5 g dry filter cake,
4 g oil with 0.86 g asphalt = 21%.

We tried heavy gasoline as a presettling agent and later washing with light gasoline, since hot oil may have to be processed, for which light gasoline is less suitable for the first stage when working without pressure. However, we did not use hot solutions in this experiment, which is to be tried in proposal III.

III. Proposal to Recover Electrode Coke.

Assumption: According to Dr. W. Jäckh, the filtration of the letdown with heptane at temperatures above 200°C and elevated pressures is possible with light gasoline -90°C (6434 or 5058 gasoline) or paraffinic gasoline in general.

Conclusion: According to Dr. Jäckh, the letdown is filtered free of ash when adding 1.5-2.0 parts/wt. gasoline. The residue is removed.

According to Löcker, the filtrate is mixed with pulverized, ash-free coke, possibly additional gasoline added, cooled, stirred and, if possible, filtered directly or after first using process Scheme I.

The ash-free filter residue produced (coke and asphalt) is freed of gasoline and forms the raw material for electrode coke/ The deasphalted, ash-free oil is used for fuel or pasting oil.

C.H. Material Balances

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COAL BALANCES AFTER FEBRUARY 1944.

Ludwigshafen, June 1, 1944.

Beginning with February the Pölitz operating control reports will contain analyses of the L.T.C. residue and L.T.C. gases, instead of the analyses of pasting oil + film oil (Gleitöl) in the input and letdown and total catchpot product in the output, from which data the conversion could be calculated.

The calculation of the conversion, therefore, now contains a certain doubtful quantity. The conversion is possibly lower, never higher(1), and the item "Unverifiable losses" is then correspondingly lower. The latter item also contains the C-losses by circulating gas leaks, since the methane and CO-content of the chemically bound and dissolved make-up gases are deducted before gasification.

The C-content of these "Unverifiable losses" can only be estimated.

The Pölitz C-balances give a lower C-deficit than the attached balances. This difference is partly explained by what is said above about conversion and losses(1), and partly by the lower yields from the added heavy oils established by Pölitz (2).

The low H_2-content of the liquefaction in February deserves particular attention, the low chemically bound H_2 is proportional to it.

(1) - For the established conversion a C-content of the hy-residue of over 100% is calculated from the Pölitz analyses. Obviously, the conversion must be lower or the analyses are in error.

(2) - The heavy oil addition is calculated from the input and output. These heavy oils consist of bit. coal tar oils, gas producer tar, petrol. catchpot heavy oil and letdown distillate, together with coal catchpot heavy oil: 12.5% heavy oil from outside oils and 87.5% heavy oil from the coal catchpot.

Table I

Pölitz

Coal Balance for March 1944.

Coal Factor

1091 kg dry Hydr. Coal with
6.3% Ash/dry coal & 2.2%
H_2O on dry coal
1000 kg pure coal

46 kg light ends
535 kg s-gasol. + mi oil

581 kg
\- 41 kg fr. 48 kg hy-oils at
85% Yield
540 kg

H_2-Consumption

Chem. bd.	850 m^3 H_2	100%
Dissolved	240 "	55% H-C. 1-4 + N_2
Loss	30 "	(Estim.)
	1120 m^3 H_2	100%

Loss Calculation.	Lu	Pö
L.T.C. Residue	127.5 kgC	146 kg C
L.T.C. Gas	6.5 "	6.5 "
unverifiable (incl. circ. gas loss)	46 "	21.5 "
	180.0 kgC	174.0 kg C

1000 kg P.C. 82% C 3.85 H Avail.
67 " Ash
43 " Cat. waterfree
24 " Water
1134 kg Dry coal + Cat.
1530 kg Paste Oil + Film Oil (82 kg. solids = 5.4%)
2664 kg Tot. Paste w. 44.8% Solids
65 kg Flush. Oil w. 40% Thick Paste 52.5% Solids
2729 kg Tot. Inj. Without H_2O & H_2 60% Thin Paste 41.5% Solids

C-Conversion 92.1%; 21.2% Gasif./Charged C
P.C.-Conversion 92.8%; 23% Gasif. Converted C
27.2% Gasif/oil yield + gasif.

755 kg C Converted

174 kg C Gasif. w. 3.3% as CO & 3.65% as CO_2
W.C. in H.C. 1.95

501 - 671 kg HD-Oil Yield 86.4% C

131 kg Loss 89% C (assumed)

540 kg Oil Yield → 43 kg light ends 86.1% C
→ 60 kg Gasol
→ 437 kg M-Oil
} 11.29 H Avail.

Table I - Continued

T-272

Residue Processing

72 kg	Hy-Residue, 90%C (assumed)
67 "	Ash & Coal
43 "	Cat.
82 "	Solids fr. Paste Oil & film Oil
264 kg	Solids in Letdown.
925 "	Oil
1189 kg	Letdown 22.2% Solids
230 kg	Pre-cool Oil
331 kg	C.P. Heavy Oil
1750 kg	

Distillation (+light ends)

1208 kg	C.P. Product
13 "	After Cool. Oil
1221 kg	
103 kg	gasol. + light ends
437 kg	Mi-Oil
681 kg	Heavy Oil

331 kg	65 kg	16 kg	269 kg
Thinn. Oil	Flush.oil	to L.T.C.	To Paste Oil

Pasting Oil + Film Oil

1261 kg	Centrif. Oil
269 kg	C.P. Heavy Oil
1530 kg	

Centrifuging

1261 kg Centr. oil

489 kg	Residue 37% Solids.
4 kg	Cat.
16 kg	C.P. Heavy Oil
509 kg	

L.T.C. 74.4% Yield

230 kg	Pre-cool. Oil
13 kg	After-cool. oil
243 kg	

11 kg Gas

68 kg	Coke + Oil
186 kg	Solids
254 kg	

Losses

79 kg	in L.T.C.
52 kg	unverifiable, incl. circ. gas loss.
131 kg	

TABLE II Pölitz

Coal Balance of February 1944.

Coal Factor

1083 kg t/ann.	Hydr. Coal w. 6% Ash/dry coal & 1.8% Water on dry Hydr. Coal
1000 kg	Pure coal
39 kg	Light ends
549 kg	s-gasol. + Mi-oil
588 kg	
- 63 kg	fr 74.5 kg Heavy Oil (85%)
525 kg	

1000 kg	P.C. 81.8% C 3.61 H avail.
64 kg	Ash
42 kg	Cat. Water-Free
20 kg	Water
1126 kg	dry coal 1.8 + Cat.
1504 kg	Pasting & Film Oils (74 kg Solids = 4.9%)
2630 kg	Tot. Paste with 44.8% Solids 40% Thick Paste w. 53.3% Solids 60% Thin Paste w. 41.7% Solids
113 kg	Flush Oil
2743 kg	Tot. Inj. without H_2 & H_2O

C-Conversion 91.5%; Gasif/Charged C 22.2%
P.C. " 92.3%; Gasif/Conv. C 24.3%
Gasif/Oil yield + Gasif. 26.3%

749 kg Conv. C.
182 kg C Gasif. 3.3% as CO & 3.8% as CO_2

H_2-Consumption

Chem. bd.	745 m^3	H_2 100%/t p.c.
Dissolved	250 "	55%/H-C. 1-4 + H_2
Loss	30 "	(Estim.)
	1020 m^3	H_2 100%/t p.c.

w.6. in H-C. 1.94

Loss Calculation.	Lu	Pö
L.T.C. Residue.	126 kgC	142 kg C
L.T.C. Gas	5 " "	5 " "
unverifiable, incl. circ. gas loss	44 " "	25.5 kg C
	175 kgC	172.5 kg C

567 kg C-644 kg HD Oil Yield
119 kg Loss 89% C. (Assumed)

525 kg Oil Yield	66 kg	light ends	87.84%C
	104 kg	Gasol-165	9.99
	355 kg	Mi-Oil-325°	H Avail.

Table II - Continued

Residue Processing

77 kg hy residue 90% C (assumed)
64 kg Ash fr. Coal
42 kg Cat.
74 kg Solids fr. Pasting & Film Oils
257 kg Solids in Letdown
957 kg Oil
1214 kg Letdown 21.2% Solids
218 kg Pre-cool. Oil
215 kg C.P. Heavy Oil
1647 kg Centrifuge mixture 15.6% Solids

Distillation (+ light ends)

1184 kg C.P. Product
14 kg After cool. oil
1198 kg

3 kg Gas
170 kg Gasol. incl. light ends
355 kg Mi-Oil
670 kg Heavy Oil

327 kg To pasting oil, 113 kg Flush. Oil, 215 kg Thinn. Oil, 15 kg To L.T.C.

Losses

L.T.C.	70 kg
unverifiable	49 kg
	119 kg

Centrifuging

1177 kg Centr. Oil

470 kg Residue 38.5 Solids
4 kg Cat
15 kg C.P. Heavy Oil
489 kg

Pasting - Film Oils

Centrifuge Oils	1177 kg
C.P. Heavy Oil	327 kg
	1504 kg

L.T.C. 77% Yield
(75.5% Without cat. oil

218 kg Pre-Cool Oil
14 kg After Cool. oil
232 kg L.T.C. Oil

10 kg Gas

60 kg Coke + oil
187 kg Solids
247 kg

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T-273

KCBraun
3/17/47

DIESEL OIL PRODUCTION IN BITUMINOUS COAL HYDROGENATION PLANTS.

By Oettinger, Ludwigshafen, 5. June, 1941

Table I indicates same possibilities of diesel oil production in a bituminous coal hydrogenation plant.

Summary:

I. The maximum quantity of diesel oil that can be produced in a bituminous coal hydrogenation plant of a capacity of 200,000 t/ann. auto gasoline is 125,000 t/ann; 82,000 t/ann. auto gasoline are produced with it. With a production of about 100,000 t/ann. aviation gasoline, the diesel oil produced is about 90,000 t/ann.

If a bituminous coal hydrogenation plant with a capacity of about 200,000 t/ann. auto gasoline and 200,000 t/ann. fuel oil is converted to diesel oil production, only 78,000 t/ann. diesel oil, besides about 125,000 t/ann. auto gasoline and 200,000 t/ann. fuel oil can be produced, due to the increased quantity of liquid phase gasoline. When aviation gasoline is produced, the above diesel oil quantity drops to about 55,000 t/ann.

II. In the production of diesel oil the quality of the gasolines produced with it deteriorates in proportion to the diesel oil quantity (octane number of the aviation gasoline estimated about 71 M.M., octane number of the auto gasoline 55-60).

III. The 6434 vapor phase is partially or entirely down.

IV. The diesel oil produced has an cetane number of 35 to 40 (thinned or concentrated prehydrogenation catalyst).

The pour point of the diesel oil is very low, below -35° C, though its viscosity at 1.08° E/20° C is also low.

V. If diesel oil is to be produced in a bituminous coal hydrogenation plant, we must provide:

a.) separate product distillation for 5058 and 6434.

b.) the 5058 c.p.p. distillation column must be so laid out that a light gasoline -120° C, an intermediate fraction 120-180°D and middle oil > 180° C can be cut out.

c.) lye and water wash for the diesel oil.

d.) adequate intermediate and finished product tanks.

The attached Table 1. shows some possibilities to take diesel oil out of the vapor phase, starting from 1000 kg of liquid phase gasoline and middle oil.

In case a.), the liquid phase is running gasoline and middle oil, in case f.), gasoline, middle oil and heavy oil (fuel oil).

In each case the normal operating method, running auto and/or aviation gasoline, is compared with an operating method (Fahrweise), in which diesel oil is taken out after saturation (prehydrogenation). Besides diesel oil, auto and/or aviation gasoline is produced.

For case a.), no fuel oil, the following production possibilities exist for a plant producing 200,000 t/ann. auto gasoline:

Production in t/ann.				
Auto gasoline	200,000		82,000	
Aviat.gasol.O.N. 87	-	180,000		100,000
Diesel Oil			126,000	93,000
Total Production	200,000	180,000	208,000	193,000

For case b.), fuel oil, the following approximate production possibilities exist:

Production in t/ann.				
Auto gasoline	200,000		127,000	
Aviat.gasol. O.N. 87		185,000		134,000
Diesel Oil			78,000	54,000
Fuel Oil	200,000	200,000	200,000	200,000
Total Production	400,000	385,000	405,000	388,000

As may be seen from Table 1, in the production of auto gasoline and diesel oil the saturation gasoline is taken out as auto gasoline, the gasoline is not quite up to standard ("siedegerecht,"-too little low boiling constituents), and the middle oil boiling above the gasoline is taken out as diesel oil (maximum diesel oil quantity). The 6434 stalls are idle in this case. If a part of the diesel oil is run over 6434, the quantity and quality of auto gasoline can be correspondingly improved.

If aviation gasoline is to be produced besides diesel oil, the 5058 and 6434 products should properly be distilled separately, and in such a manner that the 5058 product (Abstreifer) is split into gasoline to about 120°C, a heavy gasoline 120-180°C and middle oil>180°C. The heavy gasoline and a part of the middle oil are processed to aviation gasoline over 6434 so that its mixture with the saturation gasoline to about 120° will give the finished aviation gasoline. The aviation gasoline so produced should be nearly equal in quality to VT705 gasoline.

Generally speaking, the 6434 stalls are either partially or entirely inoperative when saturated middle oil is taken out as diesel oil.

DIESEL OIL QUALITY

Table II shows the properties of some B-middle oils produced in 6 and 1 liter converters by prehydrogenation of bituminous coal.

It indicates that the B-middle oils from prehydrogenation of bituminous coal liquefaction middle oil have a cetane number of about 35. In saturating with catalyst 5058 a cetane number of about 40 may be obtained. The bituminous coal diesel oils have a very low pour point, below -35°C, though the viscosity at 1.08° E/20°C is somewhat low.

Furthermore, it may be necessary to provide a lye and water wash for such diesel oil produced in a bituminous coal hydrogenation plant.

Table I

Possible Diesel Oil Production in Bit. Coal Hydrogenation Plant

	a) 1000 kg L. Ph. Gasol. + Mi-Oil to Gasol + Mi-Oil 505S	or	or	or	b) 1000 kg L. Ph. Gasol. + Mi-Oil to Gasol. + Mi-Oil + Fuel Oil 505S	40% L.Ph. Gasol. - 200°		
kg G.P. Product	962	962	962	962	950	950	950	950
kg Gasol. EP	378 - 180°	286 - 150°	378 - 180°	190 - 180°	565 - 180°	520 - 150°	586 - 180°	360 - 120°
kg Heavy Gasol.	—	—	—	188 120-180°	—	—	—	226 120-180°
kg B-Mi-Oil	580 180°	672 150°	580 180°	580 130°	360 180°	426 150°	360 180°	360 180°
6434			—	(1)			—	(1)
kg Gasol. EP	540 - 180°	542 - 150°	—	271 - 150°	335 - 120°	342 - 150°	—	258 - 140°
End Products								
kg Auto Gasol.	918	—	378	—	921	—	565	—
kg Aviat. Gasol.	—	[illegible]	—	461	—	862	—	618
kg Diesel Oil	—	—	580	425	—	—	360	250
Tot. End Products	918	[illegible]	958	886	921 (x)	862 (x)	945 (x)	868 (x)
				(1) Make-up oil for 6434 188 kg/heavy Gasol. + 155 kg B-Middle Oil				(1) Make-up oil for 6434 226 kg Heavy Gasol. + 110 kg B-middle oil.

(x) Also 920 kg L-Phase Product Heavy oil as fuel oil.

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TABLE IX

Preparation of D-Middle Oils from Prehydrogenation of Bit. Coal Liquefaction Middle Oil.

Saturation Catalyst	5058	5058	5058	5058	5058/ 7846	5058/ 7846	7846	7846
% Gasol in Product	53	37.3	23.4	20.5	23.4	27	27	44
D-Middle Oil								
Spec. Grav.	0.861	0.851	0.876	0.858	0.878	0.872	0.876	0.876
Aniline Point °C	53	49	41	34	31	38	38	41
Initial Boil °C	212	190	196	193	189	200	187	185
E.P. °C	303	305	310	308	309	307	318	319
Cetane Number	—	43$^{(x)}$	40$^{(x)}$	38$^{(x)}$	30	37	34.5	35
Pour Point °C	—	—	—	—	below -35°	below -35°	—	—
Viscosity °E/20°	—	—	—	—	1.085	1.085	—	—
% Phenols	—	0.03	0.07	0.33	0.007	—	—	—

(x) Recalculated from cetane number.

Gases

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THE HEATING VALUE OF RESIDUAL GASES IN LINDE GAS SEPARATION INSTALLATION.

Bottrop-Boy, August 15, 1937

In accordance with your request, we are enclosing a gas balance for the separation of 8,400 m^3 coke oven gas - 1,000 m^3 pressure release gas. The upper heating value of the residual gas, the gas returned from the ethylene fractions from Zweckel and the off gases of the gasol fraction are not included. Both contain appreciable amounts of ethane, and would raise the heating value of the residual gas to 5,000 kcal/m^3. The residual gas to be delivered to the glass plant in Welheim will accordingly have at least 6,200 to 6,700 kcal, depending on the method.

Signature (illegible)

Gas Balance

for the decomposition of 6.400 m^3 coke oven gas and 1,000 m^3 pressure release gas.

Constituent	Ahead of scrubber		Dissolved in scrubber water and alkali		In front of separation installation		C_2H_4 fract. incl. gasol.		CH_4-CO-H_2 fraction		N_2	
	% by Vol.*	m^3	% by Vol.**	m^3	% by Vol.	m^3	% Vol.	m^3	% Vol.	m^3	% Vol.	m^3
H_2	55.6	5219	26.0	124	57.1	5095	1.2	5	4.1	140	98.0	4950
N_2	8.8	822	4.2	20	9.0	802	0.2	1	21.2	731	1.4	70
CO	5.6	528	3.0	14	5.8	514	0.2	1	14.0	483	0.6	30
O_2	0.5	50	0.6	3	0.5	48	—	-	1.4	48	—	—
CH_4	23.3	2195	11.8	56	24.0	2139	24.3	105	59.2	2034	—	—
C_2+H_4	1.3	118	3.2	15	1.1	102	22.5	98	0.1	4	—	—
C_2+H_6	1.6	156	0.6	3	1.7	153	35.0	153	—	—	—	—
C_3+C_4	0.8	75	0.6	3	0.8	72	16.6	72	—	—	—	—
CO_2	2.5	237	50.0	237	—	—	—	—	—	—	—	—
	100.0	9400	100.0	475	100.0	8925	100.0	435	100.0	3440	100.0	5050
									H_o	6230 $\frac{kcal}{m^3}$		

*Calculated from analysis of coke oven gas: H_2 - 54.6%; N_2 - 9.2%; O_2 - 0.6%; CH_4 - 24.1%; C_2H_4 - 1.4% C_2H_6 - 017%; C_3 - C_4 - 0.3%; CO_2 - 2.8%; and the analysis of the pressure release gas: H_2 - 63.4%; CH_4 - 17.0% C_2H_6 - 9.6%; C_3 + C_4 - 5.0%; N_2 - 4.8%

According to Dr. Frese's report. 5/4/38: H_2 - 63.4; CH_4 - 17.0; C_2H_6 - 9.6; C_3-C_4 - 5.0; N_2 - 4.8; CO_2, NH_3, H_2S - 0.2.

** On the assumption that when releasing the pressure of water, half of the gases except CO_2 can be returned.

Bottrop-Boy, Aug. 26, 1938

Re: ours of 8/15/38, we wish to notify you that is has been found in the meantime, that the residual gas from Zweckel can not be returned into the residual gas from the Linde installation for some operational reasons. Nor is it possible to have the coke oven gas, set free from the water scrubber, returned to the suction side, but it can only be added to the Welheim heating gas. This will alter the gas balance but slightly.

The heating value of the gas to be sent to the glass factory will then be about 6,200 kcal.

Gas Balance

For the separation of 8,400 m^3 coke oven gas + 1000 m^3 pressure release gas.

Constituent	Ahead of scrubber *)		Dissolved in scrubber water and alkali		In front of separation installation		C_2H_4 fract. incl. gasol.		CH_4-CO-N_2 fraction		N_2	
	% by Vol.	m^3	% by Vol.	m^3	% by Vol.	m^3	% Vol.	m^3	% Vol.	m^3	% Vol.	m^3
H_2	55.6	5219	34.1	256	57.3	4963	1.3	5	4.1	138	98.0	4825
N_2	8.8	822	5.5	41	9.0	781	0.2	1	21.2	710	1.4	70
CO	5.6	528	4.0	30	5.8	498	0.2	1	14.0	467	0.6	30
O_2	0.5	50	0.4	3	0.5	47	—	-	1.4	47	—	—
CH_4	23.3	2195	16.4	123	24.0	2072	24.9	97	59.2	1975	—	—
C_2H_4	1.3	118	4.8	36	1.0	82	20.3	79	0.1	3	—	—
C_2H_6	1.6	156	1.6	12	1.7	144	37.0	144	—	—	—	—
C_3+C_4	0.8	75	1.6	12	0.7	63	16.1	63	—	—	—	—
CO_2	2.5	237	31.6	237	—	—	—	—	—	—	—	—
	100.0	9400	100.0	750	100.0	8650	100.0	390	100.0	3340	100.0	4925

H_o 6230 $\frac{kcal.}{m^3}$

*) Calculated from coke oven gas analysis: H_2-54.6, N_2-9.2; CO-6.3; O_2-10.6; C_2H_4-1.4 C_2H_6-0.7; C_3-C_4-0.3; CO_2-2.8; and of the pressure release gas: (Dr. Frese's report 5/4/38): given on the preceding table.

U. S. BUREAU OF MINES
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EXPERIENCES IN COLD PASTE INJECTION

By Schappert and Wilde, Ludwigshafen, 18 Nov. 1941

In a meeting held on November 10, 1941, the thermo-technical side of cold paste injection, first made in Scholven, was also discussed. The attached data also include an investigation into this question based on conditions in bit. coal hydr. plants.

The attached data also include a report from Scholven on experiences in operating with coal paste additions. To the comparison of Coal Stall I (quadruple converter system), operated with coal paste additions, with Coal Stall III (triple converter system), operated without coal paste additions, may be observed, that the burden on both stalls, based on reaction space, is the same. Naturally, the calculation of the conversion may not be overly accurate, because errors can easily occur in the recalculation of not neutralized to alkalinic operation. However, investigation of the pyridine -CS_2-insolubles in the letdown indicates that the quality of the letdown when operating with coal paste additions is superior to that obtained with normal operation.

Report 1589. Ludwigshafen, 13 November 1941.

INJECTION OF COLD COAL PASTE AND PASTE HEAT EXCHANGE

To heat 1 kg paste, equal to 0.400 kg pure coal, from 100°C to reaction temperature of abt. 425°C, requires a heat input of 1.0 x 0.55 x 325 = 180 kcal.

On the other hand, the heat of reaction liberates a heat equivalent to 0.4 x 0.92 x 446 = 160 kcal, if we assume that the injected cold paste is converted to the same degree as the normally injected paste (92%), and, therefore, also with the same heat of reaction, (440 kcal/kg decomposed pure coal).
Therefore, 1 kg cold paste saves only the cold gas equivalent of 20 kcal, or 0.16 m^3/kg paste = 160 m^3/t paste.

In other words:

A stall into which additional cold paste is injected, requires as much cold gas as before cold paste injection with equal thruput thru the preheater

The quantity of cold gas is, therefore, a criterion for the conversion (Abbau) of the cold paste coal. If the quantity of cold gas is materially reduced, e.g. by 3000 m^3/h with 7 t/h additional cold paste injection, we can figure that the conversion, based on the cold paste coal, has been reduced to 70%.

Consequently, the quantity of cold coal paste is not limited, or even determined, in any way by the cold gas.

If it is possible to bring the cold coal paste up to reaction temperature without disturbing the temperature of the converter in question or unfavorably influencing the flow conditions, it is at least theoretically possible to inject cold paste in whatever quantities desired. Of course, the cold paste would have to be added in small quantites in many places, though within a limited space, in order to maintain the necessary residence time, or with 4 converters, not beyond the second.

Now, according to Dr. Urban, cold paste injected in Scholven has proved to be best just before the second converter. This produces conditions in Converter II similar to those in Converter I. The hot return flow along the converter wall raises the colder mixture temperature to the reaction temperature. With this operating method the cold paste injection is limited by the mixture temperature produced, which must never be below the inlet temperature in Converter I (element 44). Attached Table I shows the calculated max. possible daily injection of cold paste into Converter II for Scholven, Nordstern, Stettin and Uppor Silesia, for 2 mixture temperatures:

a) 450°C, corresponding to 23.5 mV/40° element temp.
b) 430°C, corresponding to 22.3 mV/40° element temp.

Both temperatures are produced by mixing the contents of Converter I @ 476°C-25.0 mV with cold paste @ 100°C. What the actually permissible mixture temperature will be can be determined only in each individual case.

As shown in the table for Stettin and Upper Silesia the cold injection can be made in addition to paste heat exchange. Thick paste, which does not pass thru the heat exchanger in any case, is best suited for cold paste injection.

Only by the combination of both operating methods, heat exchange and cold paste injection, is it likely that the condition of autothermal operation will be practically attained.

In Upper Silesia, with a thruput of:

39.2 t/h thin paste
29.0 t/h thich paste, and
49000 m^3/h input gas,

thin paste and input gas are practically heated to the reaction temperature by heat exchange, or 70% of the theoretically possible heat exchange is already obtained, while in gas heat exchange at Nordstern and Scholven only 28% is exchanged.

Cold paste injection into Converter II saves additional heat, corresponding to a further heat exchange of 9%. It may be possible to repeat this kind of cold paste injection in a converter several times.

SUMMARY.

Cold paste injection reduces the necessary preheater capacity. The heat of reaction of the coal contained in the cold paste is enough to heat the cold paste, so that the quantity of cold gas is practically unchanged by the additional cold paste.

If cold paste is injected into Converter II, 3-10 t/h of cold paste may be injected, depending upon the number of converters and the thruput.

The combination, heat exchange and cold paste injection, makes it appear possible to obtain auto-thermal operation in bituminous coal stalls as well.

TABLE I

Plant	Scholven		Nordstern		Pölitz	Upp. Silesia
Reaction Volume m³	Triple 39	Quadruple 52	Triple 27	Quadruple 36	Quadruple 36	Quadruple 36
Without Colde Paste						
Paste Thruput, thick t/h	24	27	30	38	22	29.0
thin					20	39.2
Gas Input m³/h	28,000	30,000	30,000	38,000	30,000	49,000
Cold gas, Conv. I m³/h	6,000	7,000	8,000	10,000	12,000	15,000
Total Cold Gas (Outlet) m³/h	20,000	22,000	27,000	34,000	40,000	47,500
Heat Value Conv. I Cal/°C	24,400	27,050	29,000	36,900	37,000	53,200
Preheater Load (70%) kcal/h	6,700	7,500	8,300	10,500	6,700	8,600
Additional Cold Paste or taken fr. thick paste	additional		additional		Taken fr. thick Paste	Taken fr. thick paste
a) Reduction °C	fr. 476°C —450°C		(25.0 mV —23.4			
Calculated Cold Paste t/h	3.3	3.65	4.0	5.0	4.7	6.7
Total Cold Gas m³/h	19,530	21,500	26,460	33,330	34,300	39,400
Preheater Load (70%) kcal/h	6,700	7,500	8,300	10,500	3,600	7,000
b) Reduction	fr. 476°C —430°C		(25.0 mV—22.3 mV)			
Calculated Cold Paste t/h	6.2	6.9	7.3	9.4	8.2	11.8
Total Cold Gas m³/h	19,050	20,950	26,000	32,700	30,000	33,200
Preheater Load (70%) kcal/h	6,700	7,500	8,300	10,500	4,700	5,800

EXPERIENCE IN OPERATING WITH COAL PASTE ADDITIONS AT SCHOLVEN.

By Jost, Gelsenkirchen-Buer, 24 October, 1941.

As already reported by Dr. Urban on the occasion of his visit to Ludwigshafen, we have operated our Coal Stall I (quadruple converter system) with additional coal paste injected at abt. 110°C into the connecting line between Converters I and II. Normal injection into the system over the preheater was 24 t paste/h = 11 t dry coal, while 4 t additional paste = 1.8 t dry coal was injected, or a total load on the 48 m^3 converter system of 12.8 t dry coal/h, equal to a burden of 0.27. The proportion of catch pot product to letdown was not changed by this additional load. In the conversion and asphalt values also, no deterioration in hydrogenation could be detected, as shown in attached data. The advantages of this operating method appear to be considerable, considering our overloaded preheaters, because it permits an increased coal consumption of about 20%.

This experiment was run for only about 2 weeks, because of probable chlorine corrosions at the mixture point in the Tee.

In the meantime we have made a further experiment in injecting additional coal paste into the upper part of Converter I of our Coal Stall II, also a quadruple system. The paste was injected thru a sampling connection abt. 0.5 m below the cover, where we normally add some cold gas already.

We made the following observations:

All thermoelements, starting from the top, at first dropped 1-2 mV when abt. 2 tons of paste was added. Eventually even the bottom Converter Element 1 dropped from 24 mV to 22.5 mV, although the Preheater Element 44 before the converter rose from 21 mV to 22 mV, when the quantity of paste was reduced from 25 t to 22/23 t. This procedure was repeated several times with the same result.

We draw the following conclusions from these observations:

Our former belief that a strong downward flow of hot paste (Körting effect of the fresh coal paste) along the converter wall, along which the thermo-wells are also located, occurred in our converters, was at last verified. In normal continuous operations ("Beharrungszustand"-condition of equilibrium) when the paste is heated in the preheater to abt. 21 mV, the paste temperature is probably first increased to abt. 22.5 - 23 mV by its mixture with the 25 mV hot circulating reaction material. Only then does the reaction become active. In starting up a new system, at the changeover from oil to paste, the temperature is at first raised to 22.5 mV in the final preheater (Element 44) with reduced paste volume. The system then slowly rises to 25 mV in abt. an hour, while the preheat temperature almost automatically drops, possibly to 21.5 mV with increased paste injection, because the heating of the mixture in Converter I has stopped.

In the future, therefore, we shall inject our additional paste only into Converter II and utilize the circulating heat in the converter for heating the paste directly.

INJECTION OF COLD COAL PASTE INTO LIQUID PHASE CONVERTERS.

By Schönfelder, Buer-Scholven, 21 October 1941.

The Hydrogenation Division has made experiments to inject cold paste, instead of cold gas, directly into the coal converters, by-passing the preheater, and has been able to increase this quantity to 3 t/h.

The letdown of Stall I in question was compared with the letdown from the normally operating Stall III in the laboratory, with results as shown in Table II. In comparing the figures, it must be considered that Stall I operates with after-neutralization, Stall III does not. Consequently, the ash introduced with the soda must be deducted from the solids and ash content of Stall III. To 11.5 t of coal, 1.5% or 0.172 t of soda are introduced, which forms 0.190 t NaCl. ~~The coal contains 4% or 0.450 t of ash. By the addition of soda it rises in Stall III~~ to 0.450 + 0.190 = 0.64 t. It can be calculated from the analysis that 8.3 t letdown with 0.64 t or 7.7% ash has been produced. If the stall had been operated without soda additions to the paste, the ash would have dropped to 0.45 t or 5.4% and the solids to 2.11 - 0.19 = 1.92 t or 23.2% solids with 23.4% ash. Actually, the data on the analysis of Stall I show approximately the same values at 23.3% solids and 25.8% ash in the solids.

This means that conversion goes practically just as far when injecting cold paste as when operating normally.

The asphalts produced were then further examined. If the figures in Table II are recalculated for ash-free substance, we get:

the 25 mV hot circulating reaction material. Only then does the reaction become active. In starting up a new system, at the changeover from oil to paste, the temperature is at first raised to 22.5 mV in the final preheater (Element 44) with reduced paste volume. The system then slowly rises to 25 mV in abt. an hour, while the preheat temperature almost automatically drops, possibly to 21.5 mV with increased paste injection, because the heating of the mixture in Converter I has stopped.

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ASPHALT DECOMPOSITION
(Calculated for Ash-Free Substance)

	With Cold Paste Injection.	Normal Operating Method.
Soluble in Chloroform		
with 20° C neutral oil	66.2%	58.8%
with 50° C oil resin	7.1	12.7
Soluble in Pyridine		
with 20° C asphalt resin	9.0	7.7
with 50° C hard asphalt	1.1	1.1
Soluble in Pyridine - CS_2		
(asphaltene, carbene, carboide)	5.1	2.7
Insoluble in Pyridine - CS_2	11.5	17.0
Total	100.0%	100.0%

Accordingly, the letdown obtained with cold paste injection contains more neutral oils and less absolutely insoluble solids than the normal letdown.

Both experiments, therefore, indicate that conversion is at least no worse with cold paste injection than with the normal operating method.

TABLE II.

Designation of Sample: Letdown Stall I & III

Date Received: 3 October 1941

Origin: Bldg. 193

Kind of Experiment	Letdown, Stall I with cold paste after-neutralization	Letdown, Stall III Alkaline Letdown
Density @ 100°C	1.231	1.258
Softening Point	36°C	49°C
Solids	23.3 %	25.4 %
Ash in Solids	25.8 %	30.3 %
Soda	0.08%	0.47%
%/wt. to 325°	7.0 %/Wt.	1.7 %/Wt.
Asphalt Decomposition:		
Soluble in Chloroform		
with 20°C Neutral Oil	62.6 % in raw prod.	54.2 % in raw prod.
" 50°C Oil Resin	6.7 % " " "	11.8 % " " "
Soluble in Pyridine		
with 20° C Asphalt Resin	8.5 % " " "	7.1 % " " "
with 50° C Hard Asphalt	1.0 % " " "	1.0 % " " "
Soluble in Pyridine - CS_2 - (Asphaltene, Carbene, Carboids)	4.8 % " " "	2. % " " "
Insoluble in Pyridine-CS_2	16.4 % " " "	23.4 % " " "

EXPERIENCES WITH COLD PASTE ADDITIONS AT GELSENBERG.

By Becker, Ludwigshafen, 7 January, 1942.

Up to 16.5 tons of pure coal have been put thru a quadruple coal stall by the injection of cold paste into Converter 2. About 2.5 t of this is cold paste into Converter 2 and 14 t thru the preheater.

Stall 3 was operated with 40 m^3 injection, of which an estimated 34 m^3 go thru the preheater and 6 m^3 into Converter 2. Injection is made into the emergency expansion line of Converter 2. The system is primarily controlled by Element 144. A somewhat higher temperature is permitted in the converters than without cold paste injection. In Scholven, as well as in Gelsenberg, Element 144 recorded a higher temperature when cold paste was injected, which is apparently only due to the fact that less cold paste passes thru the preheater and the estimated proportion of 34:6 is not quite correct.

A characteristic picture of the temperatures in the converters with cold paste injection is reproduced here.

Element 144	20.6 - 20.8 mV	Max. Temp.	Mean Temp.
Converter 1	fr. 23.1 to 25.2, rising.	25.2 mV	24.8 mV
Converter 2	fr 24.1 to 25.3, rising.	25.3 mV	24.8 mV
~~Converter 3~~	~~Uniform @ 25.1~~	~~25.1 mV~~	~~25.1 mV~~
Converter 4	Uniform @ 24.8	24.9 mV	24.8 mV

Catchpot inlet, 22 mV
Product at hot catchpot outlet, 21.4 - 21.6 mV
Letdown " " " " , 20 mV

The quantity of cold gas is generally lower when cold paste is injected. It is divided between the individual converters as follows:

Volume of cold gas without cold paste injection	Volume of cold gas with cold paste injection.
Converter 1, 5000 m^3/h	8000 m^3/h
Converter 2, 10-11000 m^3/h	2000 "
Converter 3, 4000 "	4500 "
Converter 4, (1) 13000 "	13000 "
33000 m^3/h	28000 m^3/h

(1) These figures include the gas, which Gelsenberg injects between Converter 4 and the hot catchpot to reduce the catchpot temperature.

The stall with paste addition has so far indicated the following results:

Letdown: C.P. Product = 52%/Wt: 48%, or 48:52%/Vol.
Letdown/t coal = 1.25 t
Asphalt in letdown, abt. 17% (i.e. 1-2% higher than the average stall without added paste.
Gasol. + Mi-Oil in oil yield, abt. 88%.
Gasification, 23-24%.
Solids in pasting oil, 11.5-12%.
Asphalt " " ", 8% } for all stalls
Asphalt " tot. heavy oil, 8-10%

The asphalt content in the heavy oil rose steadily from 8 to 10% in December, due to the increased thruput. It, therefore, remains to be seen, what asphalt proportion (Asphaltspiegel) will be obtained and whether the residue can be processed without difficulty.

The converter operators like the cold paste injection. It is no more difficult to operate, in spite of the higher temperature. In fact, it is easier to operate because of the large amount of letdown.

Summary.

The thruput of a quadruple stall can be increased from 14 to 16.5 t/h pure coal by cold paste addition. That is 18%. Gelsenberg, as a whole, increases its coal processing 15 t by additional coal paste injection, which is the equivalent of saving an entire 700 atm. coal stall.

In spite of the increased load, gasoline and middle oil can be run now as before, because a somewhat higher operating temperature can be used at the same time. The proportion of asphalt increases abt. 2%.

C. H. Paste

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

REPORT ON EXPERIMENTS ON HEATING COAL PASTE WITH HOT GAS.

(Reprint of Translation From Dr. Newman)

Gelsenkirchen-Horst, December 12, 1945

A test run over a period of 10 days was made on one unit consisting of 4 reactors and a separator. The experiments were carried out for the following purposes:

1. To investigate the possibility of heating the coal paste to the starting temperature of the reaction by mixing with an economically permissible quantity of hot gas.

2. To find the minimum temperature for starting the reaction in the first reactor.

3. To study the chemical process in a reactor in which the paste is heated suddenly from the lower swelling temperature to the reaction temperature.

4. To study the behavior of coal paste of normal concentration in the paste heat exchanger (separator product against exit gas) when the paste containing a small quantity of gas flows inside the tubes, to study the heat transfer obtainable in this case and to determine the wall temperatures in the tubes and the heat transfer for the preheater tubes for heating and mixing gas to about 914°F. (420°C).

It was intended to preheat the coal paste with a small quantity of paste gas in a heat exchanger and tubular preheater. The starting temperature for the reaction was to be reached by the addition of a larger amount of process gas in the mixing tubes ahead of the first reactor without additional heating.

The tests were carried out as follows:

The coal chamber was heated as usual using 1,340,000 cu.ft./hr. of preheated fresh gas and 353,140 cubic ft./hour of heat exchanged paste gas. The amount of paste gas was increased during the starting period to control the heat exchanger temperature. On changing over to coal paste and decreasing the amount of paste gas to 141,200 cu.ft./hour the amount of oil injected could only be cut back to 11 tons/hour because further decrease lowered the heat exchanger outlet temperature from 17 mV = 644°F (conversion as given in the original) to 13-14 mV (probably iron-constantan thermocouples). This would give an over-all coefficient of only 12.3 B.T.U./hour/sq.ft. (°F). This condition was also affected by the low yield of the separator product which could have been used to improve heat economy in the exchanger by increasing the temperature difference. By reducing the concentration of solids in the reactor feed and by increasing the yield of separator product it was possible to raise the quantity of paste injected to 27.8 tons/hour. The total quantity of feed to the reactor amounted to 38.3 tons/hour. The feed of paste gas to the heat exchanger was finally raised again from 141,200 cu.ft./hour to 353,140 cu.ft./hour in order to increase the flow rate and the space velocity in the heat exchanger tubes. The addition of oil could be reduced from 11.0 tons/hour to 6.6 tons/hour and the thruput of paste was increased from 27.8 tons/hour to 33.1 tons/hour. It was, however, not possible to maintain this thruput rate without short interruptions (variations in heating value, difficulties with the paste process). This is due to the fact that even slight variations in the operating conditions which resulted in a decrease in the yield of separator product caused a decrease in the efficiency of the reactors because of insufficient heat available for transfer in the heat exchangers, the reaction then had to be started again, which was somewhat difficult.

The following conclusions can be drawn from the results of the test runs.

1. The coal chamber equipped with this preheater can be operated satisfactorily.

2. In spite of the large amount of gas (2,300,000 cu.ft.hr.) the reactor started as usual. The temperature in the first reactor rose from 25.2 - 23.4 mV (probably iron constantan thermocouple) to 25 mV. Later on it was found advisable to allow the temperature in the first reactor to rise only to about 24.3 mV in order to have sufficient cold gas for the control of the separator exit temperature which had to be kept at 23.5 mV because of the low efficiency of the heat exchanger. The heat of reaction in the first reactor was about 164-180 B.t.u./lb. of coal and lies within the limits found for other coal chambers (149-188 B.t.u./lb. of coal). This proves that coal paste can be heated with a reasonable quantity of gas (about 48,000 sq.ft./ton of coal paste) of a temperature of 680°F to a temperature sufficient to start the reaction and it is further proved that starting is not different from that of the conventionally operated units.

3. The chemical behavior is characterized by the following data. The average reactor temperature was for equal thruput about 0.3 mV lower than the regularly operated reactors. The percentage of solids and asphalt in the sludge was 20.1 and 19.8, respectively, and corresponds to normal operating values. The amount of sludge was kept at 44-49%. The middle oil content of the separator product was about 47%, which is 1.2% below the normal value but this is due to the large amount of heavy oil recycled. It was found that the experimental operation resulted in better efficiency of the centrifuge operation, the percentage of solid matter increased to 38% in the residue and decreased to 10% in the oil. This effect persisted as long as the experimental operations lasted. During this time it was possible without special effort to reduce the solid matter in the pasting oil from 10.6 to 10.0%. No change was found in the hydrogen consumption. Gas production amounted to 22% and was lower than usual. It can be concluded that the sudden heating of coal paste to the starting temperature has no detrimental effect on the processing properties of the products. It is not entirely clear if the increased efficiency of the centrifuging operation is due to the design of the preheater or separator or due to the temporary shut-down of the neighboring chamber which normally also feeds into the centrifuges.

4. Although the preheated coal paste had only a temperature of 362°F. instead of 680°F. it was possible to reach the calculated mixture temperature by increasing the amount of gas added by about 5%. Mixing of paste and gas took place in a tee in such a way that the hot gas passed into the paste through a tube of 27.6 in. length provided with numerous holes with a diameter of 0.16 in. The gas bubbles are sufficiently small to increase the heat transfer area between paste and gas and a special length of pipe for mixing is probably unnecessary.

5. The preheater capacity corresponded to the design figures. 1,940,000 cu.ft./hour of process gas could be heated to 27.0 mV (950°F). The over-all coefficient for the gas section was found on the average about 20% higher than the calculated value. The wall temperatures rose on the average from 941°F to 964°F. because of the blocking off of a section (for mixing purposes) and the increased heat input (about 1,800,000 B.t.u./hour) necessitated by the low efficiency of the heat exchanger. The fire box temperatures changed accordingly from 1101°F, (14.0 mV).. The quantity of heat transferred (18,160,000 B.t.u./hour) is about 6% higher than calculated. The conditions with respect to the coal paste section were even more favorable.

6. For the design of the heat exchanger previous experience with heat exchangers for coal paste of normal concentration was

taken as a basis. At a flow rate of about 2.58 ft./sec. for the gas paste mixture outside the tubes the over-all coefficient remained unchanged at about 51.1 B.t.u./hour/sq.ft. (°F). Running the mixture of paste with little gas inside the tubes resulted in a decrease of the flow rate to about 1.67 ft./sec. and in accordance with the rules for heat transfer a value for a coefficient of 36.8 was assumed which is 72% of the value found for the higher rate of flow. With this coefficient it should have been possible to heat the mixture to 16.5 mV = 620°F. and it had been shown that this high temperature should actually be reached with coal paste of normal concentration in the region of swelling; a temperature of 174.4 mV = 653°F. at the heat exchanger outlet had previously been reached during the regular operation of one of the other chambers. It was not possible to reach these conditions in the experimental runs. Quite unsatisfactory heat transfer results were obtained with coal paste of the usual concentration and small quantities of gas. In order to keep the unit in operation it was necessary either to drastically reduce the concentration of solids in the paste (by the addition of 6.6 tons/hour of oil) or by increasing the quantity of paste gas to at least 353,140 cu.ft./hour. In spite of these measures only temperatures of 15.8-16.0 mV (608°F.) instead of the intended 16.6 mV (626°F.) and film coefficients of 30.7 instead of 36.8 were reached. The addition of 11.0 tons of oil and 141,200 cu.ft./hour of gas gave the same film coefficients and exchanger exit temperatures as the addition of 6.6 tons of oil and 353,140 cu.ft./hour of gas.

The quantity of heat exchanged amounts to 8,310,000 B.t.u./hour corresponding to 93% of the calculated quantity; only about 70% of these were transferred to the coal paste. The remainder was used for heating the additional 2.2 tons/hour of oil and 247,000 cu.ft./hour of gas, which means a useless expenditure of 1,440,000 B.t.u./hour and a loss of about 7.7 tons of coal paste.

This unfavorable behavior of the heat exchanger cannot be explained by the change to flowing the coal paste inside the tubes rather than outside because no fundamental difference exists for these two methods of operation as shown by the experience of the Pölitz plant. The presence of only a small quantity of gas also can have no effect, since the heat exchanging surfaces are wetted by paste in any case and the heat has to pass through this film to enter the bulk of the mixture. In the paste section of the regular preheaters over-all coefficients of 66.3 to 81.8 (calculated on internal surface) have been found. Consequently, the effect of the rate of flow and the distribution of the paste over the total number of tubes has to be clarified.

The effect of the rate of flow is much greater than expected. During a test on one of the units the over-all coefficient fell from 61.1 to 28 B.t.u./hour/sq.ft. (°F) by reducing the flow velocity from 2.53 to 1.74 ft/sec. by means of reducing the throughput to 27/6 tons (gas volume 1,080,000 cu.ft./hour, unchanged); these values indicate that gas and coal paste do not have the same velocity. In Pölitz the same heat transfer values as in regular operation are obtained when running the paste inside the tubes, in spite of the reduced exchanger surface, because the velocity of flow could be increased as required. Downward flow should therefore be advantageous, because in this case the paste flows faster than the gas due to the buoyancy of the gas. Since this effect is not noticed with the exchanger of the test unit, the reason for its low efficiency seems to be in the distribution of coal paste over the heat exchanger tubes. When operating the exchanger in such a way that the paste flows outside of the tubes the entire diameter of the exchanger is filled. In the case where the paste flows inside the tubes upwards there is a possibility that the small quantity of dispersed gas rises only in the center tubes where it reduces the density of the paste column, whereas the outer tubes contain only paste or paste with very little gas. The difference in density counteracts the pressure differential causing flow and reduction or stoppage of flow results, which means elimination of the efficiency of the outer tubes. The concept that the tubes fill uniformly in the case of upward flow is only valid for the moment of the first injection of oil and cannot be applied to continuous operation.

When using downward flow inside the tubes, differences in density and pressure add, which results in equalization of flow, and paste without gas can also flow because of its weight. The difficulties with uniform distribution of the paste on the upper exchanger section caused by the high entrance velocity of the paste can be overcome by the installation of distributors of the kind used in absorbers and distillation columns.

Calculations

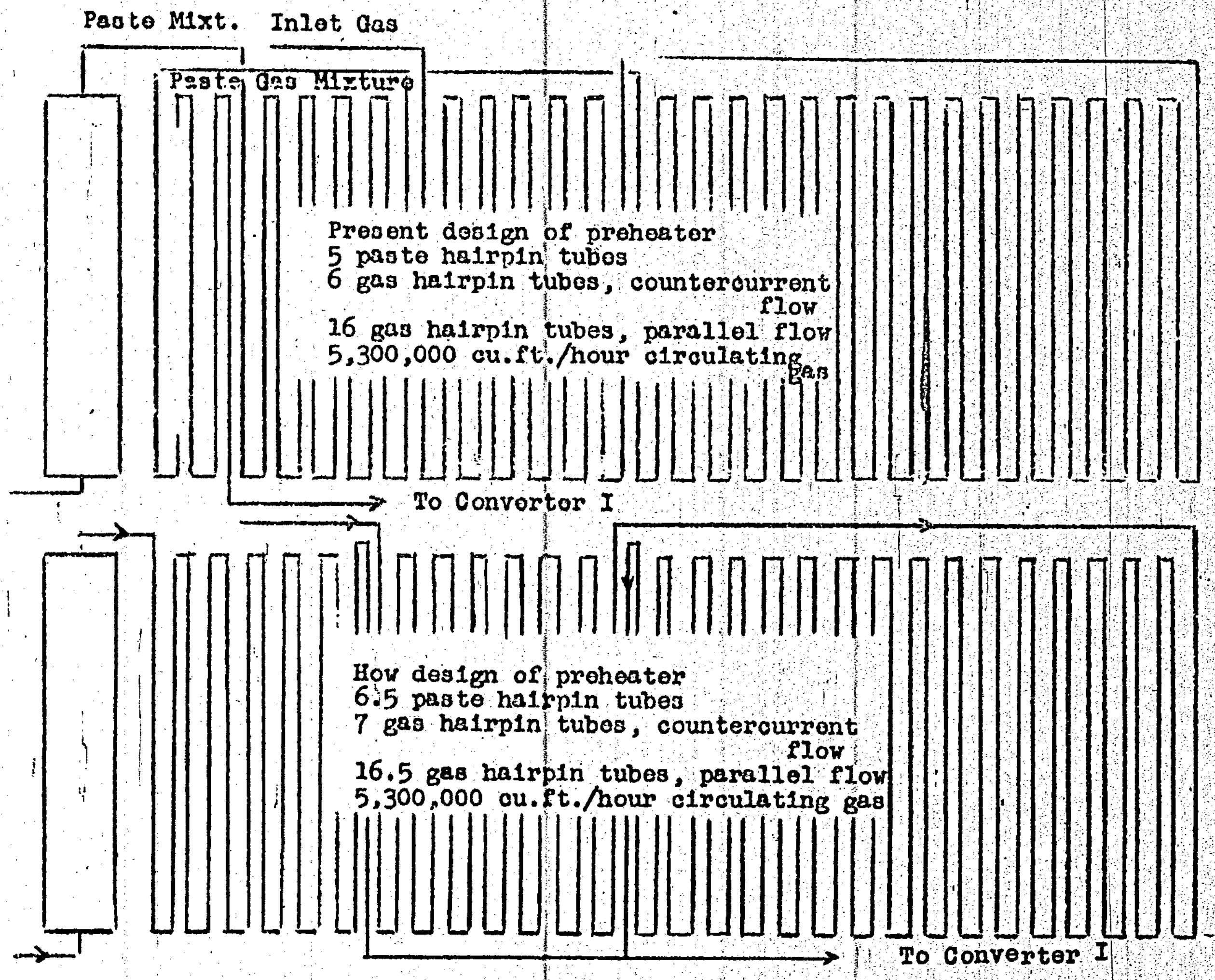
The entire gas-paste mixture with a heat capacity of 42,300 B.t.u. has to be heated in the first reactor from 779°F. to 878°F. = 99° which results in the absorption of 4,180,000 B.t.u./hour; to this has to be added 1020 B.t.u. x 878°F. - 122° F. = 774,000 B.t.u./hour. For 105,900 cu. ft/hour of cold gas and 180,000 B.t.u./hour for loss by radiation giving a total of 5,134,000 B.t.u./hour. This quantity of heat is produced from 28,500 lbs. of coal which corresponds to a heat of reaction of 180 B.t.u./lb. of coal.

Heat transfer data.

Calculated	Experimentally Found
1) Heat exchanger.	
Material to be heated: 39.7 tons/hour of paste + 4.4 tons/hour of oil + 108,000 cu.ft./hour of paste gas = 23,140 B.t.u. to be heated from 212°F. to 626°F. = 9,550,000 B.t.u./hour (9,720,000 B.t.u. including radiation loss). Material heat exchanged: 2,540,000 cu.ft./hour exit gas + 23.2 tons/hr. separator product + 1.1 tons/hr. water = 40,000 B.t.u., to be cooled from 824° F to 181°F. = 9,720,000 B.t.u./hour. Over all coefficient: 37.8 B.t.u./sq. ft./hour (°F). Exchanger surfaces: 2020 sq. ft.	Material to be heated: 33.1 tons/hour of paste + 6.6 tons/hour of oil + 363,140 cu.ft./hour of paste gas - 23,600 B.t.u., to be heated from 205°F. to 590°F. = 9,610,000 B.t.u./hour (9,640,000 B.t.u. including radiation loss). Material heat exchanged: 2,610,000 cu.ft./hour exit gas +20.9 tons/hour separator product + 1.1 tons/hr of water - 37,600 B.t.u., to be cooled from 642° F. to 603°F. = 9,640,000 B.t.u./hr. Over-all coefficient: 30. B.t.u./sq. ft./hour.
2) Preheater	
a) Gas section: Parallel flow. Material to be heated: 1,835,000 cu. ft./hour of gas = 17,700 B.t.u., to be heated from 641°F. to 914° = 6,600,000 B.t.u./hour. Material heat exchanged: 5,300,000 cu.ft. B.t.u. to be cooled from 1101°F. to 968°F. = 6,660,000 B.t.u./hour. Over-all coefficient: 1.9 B.t.u./sq.ft/hour (°F.) Max. tube temperature = 941°F. = 11.3 mV Heating surface: 36,600 sq. ft.	Material to be heated: 1,940,000 cu.ft./hour of gas = 18,700 B.t.u., to be heated from 634°F. to 932°F. = 7,075,000 B.t.u. Material heat exchanged: 6,300,000 cu.ft./hour - 49,500 B.t.u., to be cooled from 1119°F to 975°F. = 7,130,000 B.t.u./hour. Overall coefficient: 2.23 B.t.u./sq.ft/hour. Max. tube temp: 954 = 11.6 mV Heating surface: 34,500 sq. ft.

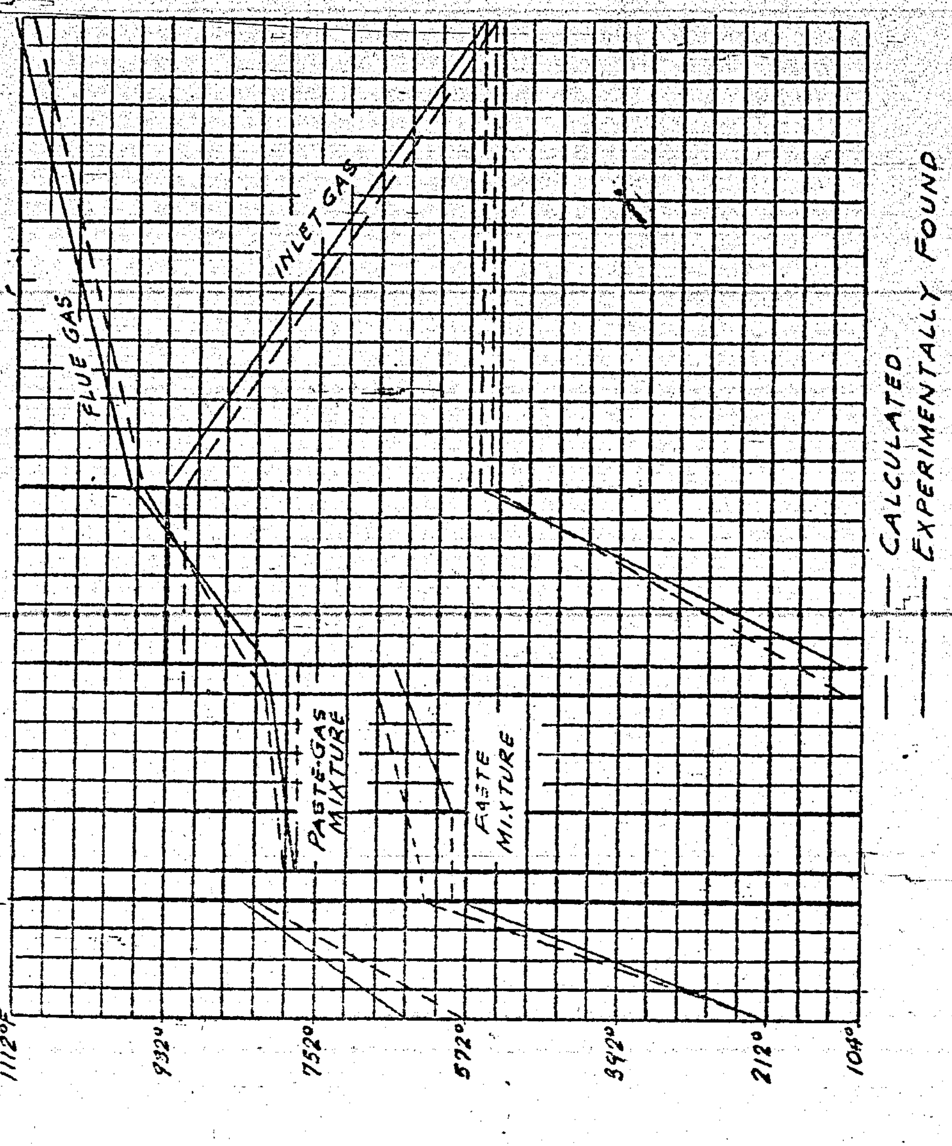
Calculated	Experimentally Found
2) **Preheater** (continued)	
b) Gas section: countercurrent flow Material to be heated: 1,635,000 cu.ft./hour of gas = 17,700 B.t.u., to be heated from 122°F. to 641°F. = 7,390,000 B.t.u./hour, Material heat exchanged: 3,300,000 cu.ft./hour of recycle heating gas = 49,600 B.t.u., to be cooled from 938°F. to 817°F. = 7,430,000 B.t.u./hour. Over-all coefficient: 1.96 B.t.u./sq.ft./hour. Heating surface: 16,100 sq. ft.	Material to be heated: 1,940,000 cu.ft./hour = 18,700 B.t.u., to be heated from 122°F. to 654°F. - 8,090,000 B.t.u./hour. Material heat exchanged: 6,300,000 cu.ft./hour of recycle heating gas = 49,500 B.t.u., to be cooled from 875°F. to 811°F. = 8,100,000 B.t.u./hour hour. Over-all-coefficient: 2.32 B.t.u./sq.ft/hour. Heating surface: 12,920 sq.ft.
c) ~~3)~~ Paste section: countercurrent flow Material to be heated: 39.7 tons/hour of paste + 4.4 tons/hour of paste gas- 23,140 B.t.u., to be heated from 626°F. to 680°F. = 1,250,000 B.t.u./hour. Material heat exchanged: 5,300,000 cu.ft./hour recycle heating as - 49,600 B.t.u., to be cooled from 817°F. to 790°F. = 1,350,000 cu.ft./hour. Over-all coëfficient: 1.31 B.t.u./sq.ft./hour. Heating surface: 14,000 sq. ft.	Material to be heated: 33.1 tons/hour of paste + 616 tons/hour of oil + 353,140 cu.ft./hour of paste gas - 23,600 B.t.u., to be heated from 690°F. to 662°F. - 1,696,000 B.t.u. Material heat exchanged: 5,300,000 cu.ft./hour recycle heating gas - 49,500 B.t.u., to be cooled from 811°F. to 777°F. = 1,710,000 B.t.u./hour Over-all coefficient: 2.06 B.t.u./sq. ft./hour. Heating surface: 10,704 sq.ft.
3) **Mixing temperature** Gas: 1,630,000 cu.ft./hour = 17,700 B.t.u. at 914°F. = 15,640,000 B.t.u./hour. Paste: 23,140 B.t.u., at 680°F. - 16,000,000 B.t.u./hour. Gas-paste mixture: 40,840 B.t.u., at 779°F. - 30,600,000 B.t.u./hour. The mixture temperature is accordingly 779°F. Preheater losses: 371,000 sq.ft. flue gas of 3600 B.t.u. Heating gas requirements: 15,300,000 B.t.u./hour 27,000,000 B.t.u./hour - 43,300,000 B.t.u./hour, about equal as in normal operation without paste heat exchangers. Efficiency of preheater: 65%	Gas: 1,940,000 cu.ft./hour = 18,700 B.t.u., at 932°F. - 16,830,000 B.t.u./hour. Paste: 23,600 B.t.u., at 662°F = 14,850,000 B.tuu./hour. Gas-Paste mixture: 42,300 B.t.u., at7779°F. as is in agreement with the calculation: the heat was, therefore, trans: ferred by mixture with theoretical efficiency. Preheater loss: 424,000 sq.ft flue gas of 4000 B.t.u., at 777°F. - about 3,100,000 B.t.u./hour. Heating gas requirements: 2,000,000 B.t.u./hour Efficiency of preheater: 84%

T-276
SK-1

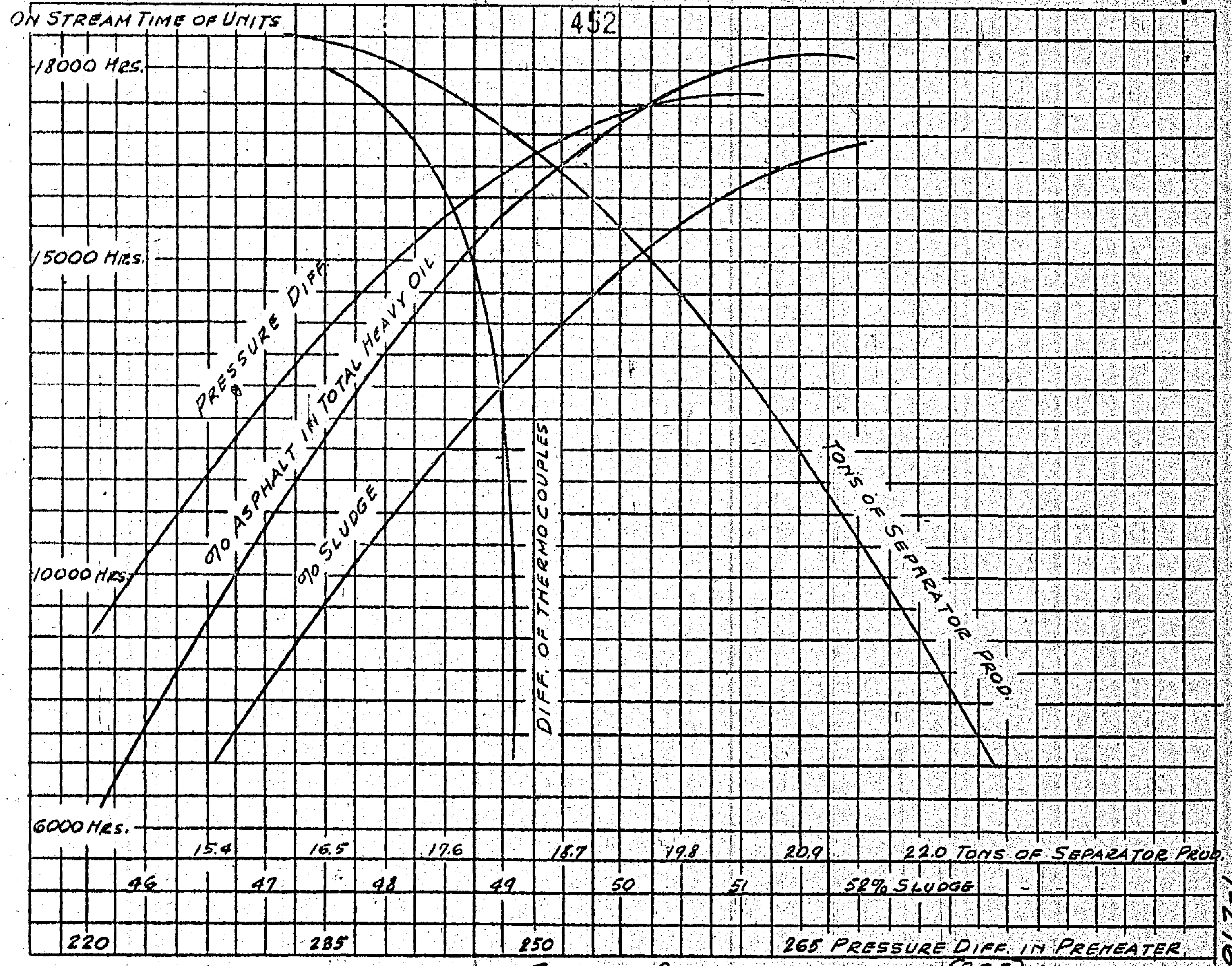


Present design of preheater
5 paste hairpin tubes
6 gas hairpin tubes, countercurrent flow
16 gas hairpin tubes, parallel flow
5,300,000 cu.ft./hour circulating gas

How design of preheater
6.5 paste hairpin tubes
7 gas hairpin tubes, countercurrent flow
16.5 gas hairpin tubes, parallel flow
5,300,000 cu.ft./hour circulating gas


1112°F
932°
752°
572°
392°
212°
104°
FLUE GAS
INLET GAS
PASTE-GAS MIXTURE
PASTE MIXTURE
CALCULATED
EXPERIMENTALLY FOUND

SKETCH - 2


ON STREAM TIME OF UNITS
18000 HRS.
15000 HRS.
10000 HRS.
6000 HRS.
PRESSURE DIFF.
% ASPHALT IN TOTAL HEAVY OIL
% SLUDGE
DIFF. OF THERMOCOUPLES
TONS OF SEPARATOR PROD.
15.4
16.5
17.6
18.7
19.8
20.9
22.0 TONS OF SEPARATOR PROD.
46
47
48
49
50
51
52% SLUDGE
220
235
250
265 PRESSURE DIFF. IN PREHEATER (P.S.I.)

SKETCH 3

453

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-277

THE PHYSICAL FOUNDATIONS OF THE LIQUEFACTION AND RECTIFICATION OF GASES.

By H. Hausen,

(Apparently from an anniversary publication "50 Jahre Kältetechnk", pp. 135 -- 162: Year of publication and editor's name not given).

Liquefaction of Gases.

The liquefaction of gaseous substances, presumably under atmospheric pressure and at room temperature, is bound up with two requirements: an appreciable increase in density, and reaching a definite temperature range, depending on the nature of the substance to be liquefied, limited from above by the critical temperature of the substance, and by its freezing point from below. Gaseous substances, for which this temperature range lies in part at room temperature, can be liquefied by simply increasing their density, through application of pressure. Thus, at 15° C, CO_2 is liquefied under a pressure of 53 atm., NH_3 under 7.3 atm. For other gases, such as air, oxygen, nitrogen, hydrogen, the critical temperature, and therefore the whole liquefaction temperature range, is below room temperature. Such gases, accordingly can only be liqufied after being cooled at least to their critical temperature. At the critical temperature, the liquefaction takes place under a specific pressure, the so-called critical pressure, with the substance assuming a "critical" density. When the temperature is reduced to below its critical value, the pressure required will be less than the critical pressure, and at the boiling point the pressure becomes equal to the atmospheric pressure, 760 mm Hg.

Table I contains the melting point, t_m., boiling point t_b at 760 mm Hg, the heat of vaporization r per 1 m^3 of gas (measured at 15° C and 735.5 mm Hg) at the boiling point, the critical temperature, t_c, the critical pressure, p_c and the critical density d_c for a few important gases. The gases are arranged in order of the descending b.p., t_b.

Table I.

Thermal Properties of Gases.

Gas			M.pt t_m (°C)	Boil.pt. t_b (°C)	Heat of evapor. per m³ gas r. kcal/m³	Critical Points		
Name	Formula	Mol. Wt. M				Temp. t_c (°C)	Press. p_c atm.	Density d_c kg/l
Ammonia	NH_3	17.03	-- 77.9°	-- 33.4°	238	+132.4°	115.8	0.236
Carbon Dioxide	CO_2	44.00	-- 56.4°	-- 78.5°	257	+31.0°	75.3	0.46
Ethylene	C_2H_4	28.03	--169.4°	--103.9°	135	+ 9.5°	52.4	0.22
Xenon	X	130.2	--140.0°	--109.1°	128	+16.6°	60.1	1.154
Crypton	Kr	82.9	--169.0°	--151.7°	93	-62.5°	56.1	0.0775
Methane	CH_4	16.03	--183°	--161.4°	81.6	-82.5°	47.2	0.1623
Oxygen	O_2	32.00	--218.4°	--182.95°	55.7	-118.8°	51.4	0.430
Argon	Ar	39.9	--189.2°	--185.7°	61.4	-122.4°	49.6	0.5308
Carbon Monoxide	CO	28	--207.2°	--190.0°	58	-138.7°	35.8	0.311
Air		28.95		--192.0°[1] --194.4°	57.4	-140.7°	38.4	0.35
Nitrogen	N_2	28.02	--209.9°	--195.8°	54.7	-147.1°	34.6	0.311
Neon	Ne	20.2	--248.7°	--245.9°	13.2	-228.7°	27.8	0.0484
Hydrogen	H_2	2.016	--259.1°	--252.74°	8.95	-239.9°	13.2	0.031
Helium	He	4.00	--272.2°	--268.88°	0.98	-267.9°	2.34	0.0693

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1) The beginning and end temperatures of condensation of air are somewhat different (-192.0 and -194.4° C). This is explained by the fact that air is essentially a mixture of 21% oxygen and 79% nitrogen, and during liquefaction relatively more oxygen is liquefied in the beginning more nitrogen at the end. However, the more nitrogen is in the condensing mixture, the lower is its boiling point.

The critical temperature of all the gases shown in the table, except the first four, is so low, as to make it impossible to reach it with the usual refrigeration machines. The liquefaction requires a special refrigeration process, the physical foundations of which are developed below.

THE IDEAL PROCESS OF LIQUEFACTION OF GASES.

The minimum work required theoretically for the liquefaction of a gas of low boiling point will be first of all explained by the derivation of the ideal process of liquefaction of a gas from the second law of thermodynamics. As in all refrigeration process, a certain amount of cold, Q_2 must be produced at a low temperature, a certain amount of energy L' must be expended, and an amount of heat, $Q_1 = Q_2 + L'$ must be transferred to the surroundings, i.e. to cooling water at the absolute temperature T_1. The amount of refrigeration, Q_2 is in part used for cooling the gas from T_1 down to the liquefaction temperature T_2, and in part to remove the heat of vaporization. The first part of Q_2 will therefore be needed during the drop in temperature, while all of the second part at the lowest temperature. In the T,s diagram, fig. 1, where the absolute temperature T is plotted as a function of the entropy s 2), and where the cooling and liquefaction proceed at the constant pressure along the curve 1 - 2 - 0, Q_2 becomes the shaded area between this curve and the temperature T = 0.

Fundamentally, only two substances have to participate in the liquefaction: the substance liquefied, which absorbs the work L', the heat content of which is reduced by the amount Q_2, and the cooling water, which receives the amount Q_1 of heat. When the two substances are considered as a single system, we find a heat exchange only inside this system (Q_1), but none with the outside. The system as a whole undergoes therefore a adiabatic* process. The second law may therefore be used in the following form: in every adiabatic process occuring in nature, the sum of the entropies of all the substances participating in the process is increasing, and is constant only in the limiting case of reversible changes of state.

According to fig. 1, the changes of entropy of the liquefying substance is $\Delta S_1 = s_0 - s_1$.

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*The word "adiabatic" is used here in the manner commonly employed in physics, i.e. for all processes (including the non reversible) where there is no heat interchange with the outside.

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2) Entropy, like the absolute temperature T, the pressure p, the specific volume v, the internal energy u, and the heat content i, etc., is a value related to the state of the substance. It is defined by the following differential equation:

$$ds = \frac{du - pdv}{T},$$

where during the reversible change of state, i.e. while continuously under equilibrium conditions, du - pvd may be set equal to the heat added, dQ. Because of the relationship between entropy and the second law of thermodynamics, entropy acquires the nature of a universal natural law.

The increase in entropy of the cooling water, the state of which can change only reversibly during the absorption of the amount of heat Q_1, is

$$\Delta S_2 = \frac{Q_1}{T_1}$$

From the principle of entropy, we get therefore the change of entropy of the whole system:

$$\Delta S = \Delta S_1 + S_2 - s_o + s_1 + \frac{Q_1}{T_1} \geqslant 0$$

Replacing Q_1 by $Q_2 + L'$, we get, after a simple rearrangement:

$$L' \geqslant T_1 (s_1 - s_o) - Q_2.$$

The theoretical minimum of work during the liquefaction of gas is therefore:

$$L'_{min} = T_1 (s_1 - s_o) - Q_2 \qquad (1)$$

The first expression on the right side, which is equal to the heat of the cooling water $(Q_1)_{min}$ is represented in the T,s diagram Fig. 2 by the rectangle 1 - 3 - -3a - 1a - 1. L'_{min} is therefore equal to the shaded area 1 - 3 - 0 - 2 - 1. We may accordingly imagine the ideal process to happen in such a way, that the gas is first isothermally compressed from 1 to 3 at the temperature T_1, its pressure then isotropically (reversibly adiabatically) reduced from 3 to 0. In the 0 state the gas would then be completely liquefied.

It may be readily shown, that the work term, L'_{min}, calculated from this ideal process, is smaller than that derived from the reversible Carnot cycle process, where the assumption is made that the total amount of cold, Q_2, is produced at the lowest temperature T_2. We get, namely, for the reversible Carnot process,

$$L'_{Carnot} = \frac{T_1 - T_2}{T_2} \times Q_2 \qquad (2)$$

which shall not be derived here. Should we select the distance 1' - 0 in fig. 2 so large, that the unit of area of the rectangle 1' - 0 - 3a - 4a - 1' is equal to Q_2, L'_{Carnot} will be represented by the rectangle 4 - 3 - 0 - 1' - 4.

When 1 kg air must be liquefied under atmospheric pressure, and the temperature of the cooling water is 15°C, the required amount of heat

$$Q_2 = 97.1 \text{ kcal/kg},$$

and the theoretical minimum of work is,

for the ideal process: $L'_{min} = 160.7$ kcal/kg = 0.254 hph/kg

for the Carnot process: $L'_{Carnot} = 253$ kcal/kg = 0.400 " "

THE LIQUEFACTION OF GASES IN PRACTICE.

The ideal process can not be carried out in actual practice, because the required maximum pressure in 3, fig. 2, would amount to between 400,000 and 500,000 atm. for air. In actual refrigeration practice a pressure of 200 atm. is seldom exceeded. It will be shown below, that this results in but a small proportion of the air being liquefied in actual practice, in contradiction to the ideal process, and that special precautions must be taken to have the cooled but not liquefied part transmit its cold as completely as possible in a way to permit its utilization in the liquefaction. In general, these processes also operate with compression, followed by expansion.

The expansion may either be done in an expansion cylinder, with a recovery of mechanical work, or in throttling valve. The first form of expansion results in a considerably larger cooling for the same drop in pressure, than the throttling. No liquefaction should occur in the expansion cylinders, and the cold obtained by expansion must be transferred to some other gas, which liquefies under pressure. Such a transfer of cold is only possible to a limited extent, and as a result, hardly any more cold ~~may be~~ utilized for liquefaction even under the best conditions, than in the expansion by throttling. This is the explanation of the fact, that the original Linde process, which utilized exclusively the throttling expansion is still more widely used, especially in Germany, than the Claude and Heylandt processes in which expansion is done in expansion cylinders. As a result, only the Linde theory will be discussed below.

THE THOMSON - JOULE EFFECT

The temperature change produced in throttling, and obtained without the addition or removal of heat, is called the Thomson - Joule effect. When throttling is done over a large temperature range, we call it the "integrated" Thomson - Joule effect. Conversely, we call the infinitesimally small temperature changes brought about by infinitesimally small pressure changes the "differential" Thomson - Joule effect; the differential effect may be assumed in practice to equal the temperature changes resulting from 1 atm. drop in pressure.

It follows from an energy balance at the throttle, that the heat content "1" should remain constant during throttling. On the strength of the second law, we may derive for the differential

Thomson - Joule effect $= (\frac{T}{p})_i$ the relationship

$$\alpha_i = \frac{T(\frac{\partial v}{\partial T})_p - v}{c_p} \qquad (3)$$

where c_p is the specific heat at constant pressure. This equation permits us to clearly recognize, that the Thomson - Joule effect is caused solely by the deviation from the ideal gas laws; because, should we apply equation (3) to an ideal gas, we would get $\alpha_i = 0$.

Fig. 3 shows the differential Thomson - Joule effect for air, from measurements by Vogel, Noell and Hausen, as a function of the absolute temperature. The solid lines are the curves at constant pressures. The broken line to the left is the saturation curve; the upper branch applies to the dry saturated gas, the lower to the liquid. Below the bottom branch, and to the left of the critical isotherm, i.e. the vertical, passing through $T_k = 132.6°$, the air is liquid.

The relative position of the isobars shows, that the Thomson - Joule effect becomes almost generally smaller as the pressure is increased. For pressures below the critical ($p < 38.4$ atm) the Thomson - Joule effect increases steadily with dropping temperature until the saturation curve is reached, as can be seen by examination of the curve, say, for 25 atm. For pressures above the critical (> 38.4 atm), the Thomson - Joule effect also increases with dropping temperatures, but reaches a maximum, and then decreases the more rapidly, the less the pressure exceeds the critical pressure. At very high pressures and very low temperatures, chiefly inside the liquid range, the Thomson - Joule effect becomes negative, i.e. instead of a cooling during the throttling there will be heating. Intersections with the vertical zero axis represent the so-called inversion points, where the Thomson - Joule effect is changed ("inverted") from cooling to heating.

PROPERTIES OF THE STATE OF AIR.

The Thomson - Joule effect is connected with the properties of the state of air by the relationship i = constant and the equation (3), especially with the heat content and the specific volumes. These equations can therefore be used to find the values of state from the measured values of α_i. Fig. 4 shows graphical computation of the state diagram of air at low temperatures produced by H. Hausen in this way.

a) i, T diagram.

The heat content "i" is represented in fig. 4 as a function of the temperature. The lines running from below on the left to above on the right are the curves at constant pressure, with the upper straight line representing p = 0. To the left, near the bottom is the saturation range, limited by the broken saturation line.

The course of the isobars shows that at temperatures above the critical, i.e. to the right from $T_k = 132.6^\circ$, as well as inside the range of superheated vapors above the saturation range, the heat content decreases throughout with increasing pressure. The high pressure curves intersect near the critical temperature, and at still lower temperatures, the heat content increases with rising pressure chiefly to the left, below the liquid range.

The heat content in the liquid range is therefore mostly greater than the saturation pressure at the same temperature, and the isobars intersect the saturation lines at high pressures, although they have nothing to do, per se, with the saturation range.

b) T,s DIAGRAM.

In fig. 5, entropy s is plotted on the abscissas, the temperature T on the ordinates. The lines from left, below, extend to the right, above, and are constant pressure curves, while the lines intersecting the former are the curves of constant heat contents. Inside the saturation range, located in the bottom part of the diagram, are the constant pressure curves, which have but a slight slope because of the difference in the saturation temperature of the liquid and the gas (cf. table 1).

Were we to go from a high initial pressure vertically to a low final pressure, we would get the theoretical cooling at reversible adiabatic (isentropic) exhausting in an exhaust cylinder. Were we to follow, however, the drop in pressure along some curve of constant heat content, we would get the temperature changes at adiabatic throttling.

c) Pv, p DIAGRAM.

The product Pv in meter-kg/kg is plotted in fig. 6 against the absolute pressure p in kg/cm^2. This diagram permits the determination of the specific volume v in m^2/kg through the division of the value of Pv as read off by the pressure P (in kg/m^2). The solid lines, which at first fall almost throughout with increasing pressure, and subsequently rise, are the curves of constant temperatures. In the saturation range, located below on the left, the curves proceed almost vertically.

The Pv, p diagram permits one to recognize very readily the deviations from the ideal gas laws, because for an ideal gas, the isotherms would form vertical straight lines.

LINDE'S SYSTEM OF LIQUEFACTION OF AIR.

The measured values of the differential Thomson - Joule effect of air furnish the calculated values in table 2 of the integral Thomson - Joule effect, on the assumption, that with any initial temperatures T_1 and pressures p_1, the exhausting is always done to atmospheric pressure.

Integrated Thomson - Joule Effect of Air, When Exhausting to Atmospheric Pressure. Table 2

T_1 - initial temperature
p_1 - initial pressure
ΔT - cooling.

T_1	t_1 (°C)	ΔT at p_1 of 50	100	200 atm.
288°	15°	11.6°	22.5°	39.0°
253	20	16.0	30.8	55.0
223	50	24.4	42.7	71.5

Were we next to throttle from 200 atm. to the atmospheric pressure at 15° C, the cooling produced, 39° would be much too small to bring us to the liquefaction temperature of air with no aid from additional measures. However, C. v. Linde has succeeded in utilizing the throttling cooling effect, by making use of counter current heat exchangers. The effect of this counter current exchangers consists in having the compressed air cooled by the exhausted air on the counter current pass of the latter from the throttling valve, so that the exhausting starts at a lower initial temperature. In this way, the temperature behind the exhausting valve will also be lowered, which will result in an additional cooling of the compressed air. The temperatures in front and behind the exhausting valve will continue to drop, until finally some of the air will liquefy during exhausting.

Fig. 7a illustrates the simplest arrangement of the Linde liquefaction process. Between 1 and 2 the incoming air is compressed at room temperature from the atmospheric pressure p_1 to the higher pressure p_2. The compression heat is taken up by the cooling water, which may also be at the temperature T_1 between 2 and 3. The compressed air is next cooled counter-currently and exhausted to the original pressure p_1 by throttling between 4 and 5. The air liquefied in this way is removed at 0, the remainder in the vapor form enters again the counter current, and becomes again heated, ideally to the temperature T_1.

In actual practice, the compression to higher pressures is always done in several stages, and the heat of compression removed by the cooling water after each compression. Intermediate cooling results in a considerable saving in the compression energy in comparison with 7a. The more stages are used, the nearer will one come to isothermal compression, in which the work of compression is the least for a given ratio of pressures. To become independent therefore from any particular type of compressors, we shall count in the future always on isothermal compression.

The liquefaction just discussed is represented in Fig. 7b in a T,s diagram. Here, 1 to 3 represents the isothermal compression. 3 to 4 the cooling of the compressed air by counter current. The liquid portion of the air in point 5 will be in a 0 state, and in the vapor state in 6, the two are thus separated and the gaseous air again heated to the temperature T_1 by the countercurrent heat exchanger.

CALCULATION OF THE COOLING EFFICIENCY.

Each kilogram of air compressed to pressure p_2 produces a liquefied fraction y, which requires, in accordance with fig. 1 the amount of cold

$$Q_2 = y\,(i_1 - i_o) \qquad (4)$$

To find y, we shall calculate the energy balance for the liquefaction unit excluding the compressors and the coolers, and base it on the consideration, that during the operation as much energy is brought to the unit, as is taken away from it. The energy brought to it consists essentially in the heat content of the compressed air entering at the warm end of the counter current, the energy taken away is the sum of the heat content of the 1 - y kg. air, leaving the warm end of the counter-current, and of the heat content of the liquid air which leaves the unit. We obtain therefore

the energy introduced $= i_3$

the energy removed $= (1 - y)\,i_1 + y\,i_o$.

Equating the two amounts of energy, we get

$$y = \frac{i_1 - i_3}{i_1 - i_o} \qquad (5)$$

and by inserting into equation (4)

$$\underline{Q_2 = i_1 - i_3}$$

This equation claims, that the cooling efficiency depends only on the state of the air at the inlet and the outlet of the warm end of the counter-current heat exchanger, and is entirely independent of what takes place at low temperatures. It is here however presupposed that the cold is actually given off at the desired low temperature, which is almost always true in the Linde process.

Equation (6) permits also the derivation of a simple relationship between Q_2 and the Thomson - Joule effect. Were we to throttle down the compressed air from the pressure 3 to the pressure t_1, while the temperature drops by the amount ΔT of the integrated Thomson - Joule effect, while the heat content retains its value of i_3, the amount of heat $i_1 - i_3 = c_p \Delta T$ is just necessary to bring the temperature up to the initial temperature T_1 after exhausting. We obtain therefore

$$Q_2 = c_p . \Delta T,$$

i.e. the integrated Thomson - Joule effect is a measure of the cold production at the warm end of the counter current heat exchanger. There is therefore no gain in the magnitude of the cold effect in the Linde process, because throttling is done at a lower temperature, and therefore with a greater Thomson - Joule effect.

The counter current effects therefore not the amount of cold transferred, but only the temperature at which this is available.

CALCULATION OF THE EXPENDITURE OF WORK.

Fig. 7 shows that air deviates from an ideal gas markedly even at room temperature, but an accurate calculation shows never the less, that the work of compression is hardly at all affected by it. We can therefore calculate with sufficient accuracy the loss-free isothermal compression work from the equation for ideal gases

$$L' = RT_1 \ln \frac{P2}{P1} \qquad (7)$$

where R is the gas constant per kg of gas. The effective compression work is actually about 1.6 to 1.7 times as large on the average as the calculated value of L', because of the deviations of the compression process from the isotherm and because of compression losses. We shall designate this factor k, and get

$$L'_{eff.} = k\,RT_1 \ln \frac{P2}{P1} \qquad (8)$$

we have used throughout 1.69 for the k value in our computations. This value comes the closest to the usual practical guarantee factor, and is therefore sufficiently high not to be exceeded with perfectly performing compressors.

It is desired in actual practice to produce a certain amount of liquid air with the lowest possible work, i.e. to obtain a minimum value of the ratio $\frac{L'_{eff.}}{y}$. Table 3 shows this ratio computed for the case when the temperature at the warm end of the counter current exchanger $T_1 = 288^\circ$ abs $= 15^\circ C$, and that the throttling valve always exhausts completely down to 1 atmosphere.

Table 3.

Production of Cold and Expenditure of Work in the Linde Process with Simple Exhausting. Cold Requirements per 1 kg Liquid Air $i_1 - i_0 = 97.1$ kcal/kg

$p_2 =$	50	100	200 atm.
Q_2	2.8	5.4	9.5 kcal/kg
$y = \frac{Q_2}{i_1 - i_0}$	0.02884	0.0556	0.0979
L' in hph/kg	0.1220	0.1436	0.1655
$L'_{eff} = 1.69 L'$	0.2062	0.2428	0.2798
$\frac{L'_{eff}}{y} =$ = work in hph/kg liquid air.	7.15	4.37	2.86

~~This table shows, that the amount of work required per kg~~ liquid air increases considerable with increasing p_2. This is explained by the fact, that the integrated Thomson - Joule effect, and therefore also Q_2, increase almost proportionally with p_2, while the work required increases only proportionately with the ln $\frac{p_2}{p_1}$.

A comparison of the calculated values with the minimum work requirements of 0.254 hph/kg liquid air in the ideal gas process shows that even the most favorable value of 2.86 hph/kf in table 3 is too high. A further reduction in the work requirements has been done by Linde by means to be presently discussed: the high pressure circuit and the precooling.

HIGH PRESSURE CIRCUIT.

The above considerations of the approximate proportionality of the production of cold and the pressure difference resulting from throttling, while the required work depends on the pressure ratio $\frac{p_2}{p_1}$, leads to the realization, that while the amount of cold produced is approximately equally great when throttling from 150 atm to 1 atm, and from 200 atm. to 50 atm., the energy consumption will be reduced to 28% of the former case because the pressure ratio will be reduced from 150 to 4. The consumption of work can therefore be appreciably reduced per kg of liquid air by increasing the lower pressure p_1. The high pressure circuit can not however be quite conducted in the manner described, because at least the same amount of air must be exhausted as taken out of the unit in the liquid state under atmospheric pressure. This amount is further increased because when exhausting from intermediate pressure down to atmospheric, part of the air liquefied at intermediate pressure will be again evaporated. Fig. 8a shows the scheme of a high pressure circuit, in which the compressor cooler is not shown for the sake of simplicity.

Air under high pressure is shown in black, under intermediate pressure in gray, and at atmospheric pressure in white. The intake air at atmospheric pressure is compressed to the intermediate pressure p_2 between 1 and 2. At 2 this air combines with the air returning from the liquefaction apparatus, and together, with that air is compressed to the high pressure p_3 between 2 and 3. The high pressure air is next cooled in the counter current heat exchanger by the returning air, which consists in part of the air under intermediate pressure, and in part of completely exhausted air, and then throttled down to the intermediate pressure p_2 through a valve between 4 and 5. Part of the intermediate-pressure air (6) passes through the heat exchanger back to the compressor; the balance, which has either completely or partially separated as liquid air in the container 7, is expanded to atmospheric pressure through the valve between 7 and 8. During this second throttling, part again evaporates (9) and is again returned through the counter current; the rest may be removed from the arrangement in 0 as liquid air. The same amount of air as has been expanded in the second throttling valve, with the necessary addition to compensate for any possible leakages, is returned to the system at 1 in the form of fresh intake.

Fig. 8b shows the same process in the form of a T,s diagram. It is here assumed that 1 kg air is compressed at the temperature T_1 from p_2 to p_3, is counter currently cooled, and throttled to p_2 between 4 and 5. M kg is then completely expanded between 7 and 8, while 1 - M kg air under intermediate pressure (6 to 2) and y- M kg under atmospheric pressure (9 to 1) are returned through the counter current exchanger. The compression of M kg between 1 and 2 and of the total amount of air between 2 and 3 must then proceed as above at constant temperature.

The production of cold by this process is found in a similar energy balance as for the Linde process with a single expansion. The energy supplied again consists in the heat contents of the compressed air which enters at the warm end of the counter current, but the energy removed is now augmented by the heat content of the air under intermediate pressure, as it leaves the heat exchanger. We get therefore:

$$\text{energy supplied} = i_3$$

$$\text{energy removed} = y\, i_0 + (M - y)\, i_1 + (1 - M)\, i_2$$

and by equating the two amounts of energy

$$\underline{Q_2} = y\,(i_1 - i_0) = \underline{(i_2 - i_3) + M\,(i_1 - i_2)} \qquad (9)$$

We get for the loss-free compression, from equation (7)

$$L' = RT_1 \left(\ln \frac{p_3}{p_2} + M \ln \frac{p_2}{p_1}\right) \qquad (10)$$

from which the effective work, L'_{eff} can be determined from eq. (8)

We can calculate for the specific case when $p_1 = 1$, $p_2 = 50$, $p_3 = 200$ atm, $T_1 = 288^\circ$ abs (15° C) and $M = 0.2$: $Q_2 = 7.26$ kcal/kg, $L'_{eff} = 0.1143$ HPH/kg, $y = 0.0748$, and therefore

$$\frac{L'_{eff}}{y} = 1.53 \text{ hph/kg liquid air,}$$

which represents an appreciable reduction in comparison to the value 2.86 hph/kg with complete expansion from 200 to 1 atmosphere.

PRECOOLING.

The earlier considerations have shown, that the cold production was only a measure of the value of the Thomson - Joule effect at the warm end of the counter current, and that the larger effects of cooling produced at the lower temperatures of throttling have no effect. Should one desire to make use of the greater Thomson - Joule effect at lower temperatures to increase the output of cold, this will only become possible by lowering the intake temperature by using refrigeration in the counter current exchanger, i.e. by precooling the air. If the intake temperature were, i.e., cooled to - 50°, the Thomson - Joule effect, and therefore the output of cold, would nearly double in comparison with the intake temperature of - 15°. Added to this is the reduced amount of cold $i_1 - i_o$ required per kilogram of liquid air, because point 1, fig. 60* is lowered by precooling, lowering therefore also the value of i_1. With a precooling to - 50° this requirement of cold is reduced to 81.3 kcal/kg from 97.1 kcal/kg at - 15°.

Refrigeration in turn requires an additional consumption of work, but this is relatively small in comparison with the gain in the production of cold, especially if the cold of the e expanded air from the main counter current exchanger, which is still rather cold, is utilized in an auxiliary counter-current heat exchanger. The amount of cold Q_k extracted per kg of air from the precooler can be computed from the T,s diagram as follows:

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*This refers to the preceeding paper in the collection; not available.

We will use as an example the case of simple throttling. T_1 will signify as before the temperature at the warm end of the exchanger without precooling, T_1' the corresponding temperature with precooling, fig. 9. The expanded air leaving the main exchanger still contains an amount of cold $(1 - y)\ (i_1 - i_1')$. The compressed air was thereby cooled in the counter current precooler to the point 3*. To cooling machine has therefore to perform the additional cooling from 3* to 3', and

$$Q_k = i^*_4 - i'_1$$

For the counter current precooler we may use the expression

$$i_3 - i^*_4 = (1 - y)\ (i_1 - i'_1), \text{ and we get}$$

$$i^*_3 = i'_1 - (i_1 - i_3) + y\ (i_1 - i'_1)$$

and by inserting into the equation for Q_x,

$$Q_k = (i'_1 - i'_3) - (i_1 - i_3) + y\ (i_1 - i'_1).$$

From equation (6) we may write for it

$$Q_k = Q'_2 - Q_2 + y\ (i_1 - i'_1) \qquad (11)$$

where Q'_2 is the cold produced in the liquefaction process with precooling, Q_2 without precooling. According to this, Q_k equals the increase in cold production caused by precooling, and is equal to $y\ (i_1 - i'_1)$, which is needed to cool the amount of air to be liquefied, y, under atmospheric pressure from room temperature T_1 to the precooler temperature T'_1. The cold produced by the cooler is selected in practice greater than follows from equation (11), because the expanded air leaving the main counter current exchanger gives up at most 70 to 80% of the available cold.

The examples below compared to earlier computations permit us to recognize the great effect of the precooler. In these examples the precooler temperature is -50°C and the cold production of the cooler is assumed to be 850 kcal/hph, and in addition it is assumed that the cold of the expanded air, as it leaves the counter current exchanger, is completely utilized.

Table 4.

Precooling to -50° C.

	Simple expansion from 200 atm. to 1 atm.	High pressure circuit between 50 and 200 atm. M = 0.35
p_1	1	1
p_2	200	50
p_3		200
Q'_2	17.3	14.0 kcal/kg
$y = \frac{Q'_2}{i'_1 - i_0} = \frac{Q'_2}{81.3}$	0.2128	0.1722
Compressor work $(L'_{eff})_1$	0.2798	0.1453
Work of cold producer $(L'_{eff})_2$	0.0132	0.0107
$L'_{eff} = (L'_{eff})_1 + (L'_{eff})_2$	0.2930	0.1560
$\frac{L'_{eff}}{y}$	1.378	0.905 HPH/kg

It must be observed in the high pressure circuit, that M must be selected larger when there is precooling, than when there is none, because of the greater amount of air liquefied.

For that reason the improvement attained with high pressure circulation and precooling is less marked, than with no precooling, but still remains considerable. The work used, shown in the second column, 0.905 HPH/kg liquid air is the most favorable value which can be theoretically obtained in the Linde process, i.e. without taking into consideration the losses in the equipment, which will be presently discussed.

Fig. 10 shows calculations for a greater number of cases with and without precooling, with the maximum pressure always at 200 atm., and the intermediate pressure plotted on the abscissa assuming any values between 1 and 200 atm. $\frac{L'eff.}{y}$ is plotted on the ordinate, and is the work expended per kg. liquid air. An intermediate pressure of about 50 atm. is seen to be the best. The fig. shows also the curve denoting the limits of applicability (long broken line), i.e. it would be impossible to obtain all the cold produced by liquid air.

IMPORTANCE OF PRECOOLING FOR THE PRODUCTION OF LIQUID HYDROGEN AND HELIUM.

In the liquefaction of air, precooling is largely a means to effect savings in power consumption, but in the liquefaction of hydrogen and helium which can also be done by the Linde process with simple expansion it becomes an indispensable prerequisite, because the Thomson - Joule effect of these gases results in a rise in temperature at room temperatures. With hydrogen, the Thomson - Joule effect results in cooling only at temperatures below - 80° C, with helium only at around -243° C (30° abs). A sufficient production of cold is only produced when precooling has lowered the temperature to below the inversion temperatures. In the liquefaction of hydrogen the precooling is done with liquid air or liquid nitrogen, in the helium liquefaction with liquid hydrogen boiled under a greatly reduced pressure. Because of the low precooling temperatures, particular care must be used in the most perfect recovery in the auxiliary exchanger of most of the cold still contained in the expanded gases. 165 atmospheres has been found to be the preferred pressure during the liquefaction of hydrogen, and 40 atm. in the liquefaction of helium.

LOSSES IN THE LINDE PROCESS.

Compression losses have already been taken into consideration by the factor k in eq. (8). There are, however, also losses in the liquefaction unit proper, and aside from the insignificant pressure losses, the following are the principal losses of cold:

1. Exchanger losses. These result from the expansion gases in the counter current exchanger not being completely warmed up to the temperature of the incoming air, and usually leave at a temperature 1 to 2° lower, thus carrying out some of the produced cold. With a temperature difference at the warm end of the exchanger Δt_a, the exchanger loss, referred to unit of mass of the escaping expanded gases are $c_p \Delta t_a$.

2. Insulation losses. It is impossible to prevent all heat from entering the equipment from the outside, and even with the best

possible insulation, there will result some loss of cold, which is in general the larger, the smaller the unit, but the details of which will be largely determined by the execution of the installation. It amounts in air liquefaction equipment on the average to 1 - 3 kcal per kg of liquefied air.

3. Evaporation losses during the draining of the liquid air. Part of the loss is caused by the higher pressure of the liquid than the atmospheric, so that some of the throttling takes place during the draining. For this loss, only the cold contents of the evaporated air must be taken into account, without considering the heat of vaporization, because the cold content of the remaining liquid air is increased at the cost of the heat of vaporization. Vaporization losses from heat taken from the outside during the discharge of liquid depend, however, also on the heat of vaporization. On the average, 2 to 5% are vaporized during the draining of the liquid air.

These losses of cold have not been taken into consideration in the calculations shown, and the calculated values are therefore too low. When referred, e.g., to a loss of cold equal to 3 kcal/kg of the liquefied air, M is increased to 0.35 for a high pressure circulation between 50 and 200 atm., and with precooling to -50° the power consumption is increased from 0.905 to 1.15 HPH/kg liquid air.

SEPARATION OF GASEOUS MIXTURES AT LOW TEMPERATURES.

The possibility of separation a mixture of gases boiling at different low temperatures into its constituents is based on the earlier condensation of the higher boiling constituents, than of the lower boiling. True, every constituent participates from beginning to end in the condensation, but in the beginning the higher boiling constituents condense in relatively larger proportion, than corresponds to their proportion in the vapor, while towards the end the condensation the lower boiling constituents will relatively predominate. Conversely, during re-vaporization, the lower boiling constituents will evaporate first, while towards the end relatively more of the higher boiling constituents will be converted into the gaseous state. This difference in the behavior of the higher and lower-boiling constituents will have as a result, that at a constant pressure the boiling point of a mixture will become lower during a progressive condensation, and will rise during vaporization. (cf. footnote 1).

Air is composed of 20.9% by volume of oxygen, with the balance composed almost entirely of nitrogen 4/, and therefore, in accordance with what has been said above, relatively more oxygen will condense at first, relatively more nitragen towards the end, because the boiling point of oxygen is 13° higher than nitrogen. Were the air liquefied under atmospheric pressure, the first drops of the liquid formed would contain 48% oxygen, the liquid last liquefied would contain, however, but 7%. When liquefying but 20% of the initial amount, the liquid formed would contain 40.5%, while the residual gas only 16% oxygen. This explains

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4/ The percent by volume has been measured in the gaseous state at room temperature and under the pressure of 1 atm. All data given below are to be understood in this sense.

why the air liquefied in the air liquefaction equipment, in which only a part of the total air is ever liquefied, produces a liquid higher in oxygen, than the atmospheric air.

When a mixture of several constituents, e.g. oxygen and nitrogen, is in the boiling state, and the liquid and the vapors are in equilibrium, i.e. they both are at the same temperature, under the same total pressure, and with equal partial pressures of the constituents, then there are definite but different proportions of constituents in the liquid and the vapor phases. Fig. 11 shows the equilibrium compositions of oxygen-nitrogen mixtures under a total pressure of 760 mm Hg = 1.033 atm. as measured by Baly, with the compositions plotted on the abscissa and the corresponding boiling points (somewhat corrected from more recent measurements) on the ordinate. This drawing permits then to find the equilibrium composition of the vapors $z = f(x)$ for some definite composition of the liquid, designated with x. The difference from equilibrium conditions for pure oxygen is greatest at intermediate compositions, but disappears only when $x = 0$ and $x = 100\%$ of pure oxygen. Fig. 12 reproduces the different equilibrium curves at different pressures between 0.5 and 10 atm. from the latest measurements by Dodge and Dunbar, which show that the equilibrium differences become smaller at higher pressures.

We shall now discuss the different separation processes of mixtures based on the physical behavior just described.

FRACTIONATED VAPORIZATION.

In principle, the vaporization of a liquid mixture may proceed in two ways. The first method, which had been tacitly assumed, in the previous discussions, consists in keeping the whole amount of the vapor in continuous contact with the liquid, with an equilibrium formed at every instant. This process shall be briefly illustrated on an oxygen - nitrogen mixture, evaporating under atmospheric pressure; if the liquid had in the beginning the composition of the atmospheric air, $x_1 = 20.9\%$ by vol., point I in Fig. 11, the first vapors formed will contain $z_1 = 7\%$ by vol. of O_2 (point I'). Nitrogen will at first evaporate more rapidly, and the liquid will become gradually enriched in oxygen, which will also result in an increase of the equilibrium value in the vapor. The oxygen enrichment of the liquid is, however, limited by the vapor at the end of vaporization when the composition is $z_2 = 20.19\%$ (point 2') and the last liquid drop to evaporate ~~will have the corresponding composition of $x_2 = 48\%$ by vol.~~ (point 2).

A considerably higher oxygen concentration in the liquid can be produced when the vapors produced are led away periodically after certain time intervals. Several vapor fractions are then produced, of which the later will always have a higher oxygen concentration, than the former. Were we to make the fractions infinitesimally small, the vaporization process will proceed as shown in Fig. 13, in which the composition of the vapor just formed and the remaining liquid are plotted as functions of the amount evaporated. The last of these infinitesimally small fractions will then consist of pure oxygen. Fractionated vaporization can therefore produce only very minute amounts of pure oxygen.

FRACTIONATED CONDENSATION.

Conversely, should the liquid formed in the liquefaction of the originally gaseous air be removed in several fractions, liquid fractions will be obtained of varying composition, and, should we again choose to have an infinite number of fractions, the first one will contain 48% by vol. of oxygen, while the last one will consist of pure nitrogen. If the gaseous mixture is only partially liquefied, and if only one, or very few fractions, are removed, we may speak of a partial condensation.

Neither fractionation vaporization, nor fractionation condensation are suited for the economic separation of air, because of the low yield in pure constituents. On the other hand, fractionation condensation has recently acquired very great importance for the separation of hydrogen-containing mixtures, such as water gas and coke oven gas. Hydrogen boils very much lower, than the other components, as seen in Table 5, and the others can be condensed out of the mixture very perfectly, without condensing significant amounts of hydrogen. Details of this process will be illustrated on a simple example.

Table 5.

Composition of Water Gas and Coke Oven Gas.

Constituents.	H_2	N_2	CO	CH_4	C_2H_4	Higher Hydro-Carb.	CO_2
B.P. of pure constit. at 1 atm.	-252.7	-195.8	-190	-161.4	-103.9	-88.3 to + 80°	-78.5(sol
% by volume in water gas	45-52	3-7	39-44	—	—	—	3-7
% by volume in coke oven gas	50-57	6-12	5-7	22-25	1-2	3-4	2-5

Let us suppose we have a gaseous mixture composed of 70% by vol. of hydrogen and 30% of methane under a pressure of 8 atm. so that the partial pressure of methane is 0.3 x 8 = 2.4 atm. The saturation temperature of methane at this pressure is -150° C. Let us also assume, that the presence of hydrogen does not affect the saturation temperature, which is nearly correct, and that the methane condensation begins therefore at -150° C.

The subsequent progress of the condensation can be computed as follows: Measured at 15° C and under 1 atm., the gaseous mixture contains V_1 of the condensing gas and V_{11} of the non-condensing gas. Furthermore, at any temperature t below the initial condensation, the saturation pressure of the condensible gas is p_1. The amount K_1 condensed at this temperature is then determined from the partial pressure of the gas I in the residual gas, p_1, and therefore the partial pressure of the gas II is $P - p_1$. Let us assume that the ideal gas laws apply to the residual gas, in which case the amounts of gases present, $V_1 - K_1$ and V_{II} are proportional to their partial pressures, or

$$\frac{V_1 - K_1}{V_{II}} = \frac{p_1}{P - p_1}, \text{ and}$$

$$K_1 = V_I - \frac{p_1}{P - p_1} V_{II} \qquad (12)$$

In fig. 14, the partial pressure p_1 of a 30% mixture of methane and hydrogen is plotted as a function of the temperature t against the amount condensed from 100 m^3 of the mixture, K_1, computed from equation (12). The presence of hydrogen, even if it does not affect the relationship between the saturation pressure and the temperature, never-the-less results in the methane not condensing at a constant temperature, but at dropping temperatures, because of the dropping partial pressure. With this simple gas mixture, the condensation should be stopped at - 183°, because methane solidifies at -183°. In gas mixtures used industrially, there always are also some other constituents, especially carbon monoxide and nitrogen, which greatly reduce the melting point of methane, and the cooling of the mixture proceeds still further. Table 5 shows the large number of components present in coke oven gas. These components affect each other during the condensation, and the simple formula (12) may no longer be used for accurate computations.

Fig. 14, however, gives the fundamentals for the condensation processes and is therefore very well adapted to clarify the difficulties with the transfer of cold in the case of coke oven gas, and these difficulties will be discussed presently. The final products are gaseous in most cases and used at room temperatures, while the separation takes place at low temperatures, and we must transform to the freshly introduced gas the cold liberated not merely during the re-warming of the separated products, but also that of the re-evaporation of the condensate in the counter-durrent exchangers or the evaporator. This transfer of cold is most perfect when the cold necessary for the condensation of a given component is produced by the re-evaporation of the same component. One may see, however, from fig. 14, that this is only partially possible with the 30% methane - hydrogen mixture, because the liquid methane drawn off at -183° evaporates under atmospheric pressure only at -161.8° C. When 100 m^3 of such a mixture are cooled to that temperature only 20 m^3 of methane become liquefied. The additional 9 m^3 methane, which remain to be separated, can not however be condensed by the evaporation of methane, and 9 m^3 of methane can therefore not be condensed. Almost one third of the cold of the liquid methane is available at higher temperature, but can not be used. One might utilize this cold by evaporating some of the liquid methane in a vacuum. It has, however been found preferable to transform this excess of cold to a lower temperature by using a different refrigerant, in most cases nitrogen. This "nitrogen refrigerator" works accordingly on the principle of the usual compression refrigerators by liquefying nitrogen with evolution of heat under a pressure of 20 to 50 atm. at the "high" temperature of the boiling methane, and re-evaporating it after throttling to the atmospheric pressure, and have the excess of cold of the methane available at the boiling point of nitrogen, -196° C. This arrangement (patent claimed by the Linde company) operates particularly economically, when the same nitrogen is also used to make up the amounts of cold necessary to cover the losses of cold in the equipment.

The condensation process described permits one to obtain 98% hydrogen from water gas or coke oven gas, when the last portions of the gaseous mixture are cooled with nitrogen, boiled in a vacuum. Still higher purity of hydrogen can be produced if a rectification process described in the next section is made to follow the best attainable fractionation condensation.

RECTIFICATION.

The outward characteristics of rectification consist in bringing countercurrently the boiling liquid and the mixed vapors in the most intimate contact, which cause them to affect mutually their composition. In general, the liquid is made to meet the vapors by having it run down over a very large surface i.e. over many broken-up intermediate surfaces. If one of the components is present in a great excess in the vapor, and must be freed from the other components by the liquid, the rectification may also be called washing.

A two-fold equalization takes place at every place of contact of the boiling liquid and the mixed vapors: an equalization of temperature and an equalization of partial pressures of the individual components in the liquid and the vapor. The equalization of partial pressure affects also the desired exchange of these components. With sufficiently long time of contact, a state of equilibrium is produced in this locality, such as may be read off Fig. 11 for the oxygen = nitrogen mixtures boiling under atmospheric pressure.

Fig. 15 represents a perforated plate for the rectification during air separation, on which a liquid containing x_n % oxygen becomes collected, and through which a vapor with y_n % oxygen is made to rise.

It has been assumed for simplicity sake, that the composition x_n of the liquid remains unchanged in spite of the effect of the vapors upon all places of the plate, a condition which might be accomplished with an ideal mixing, e.g. with the use of a stirrer. This assumption approaches the actual conditions fairly closely, because the streaming-through of the vapors does produce a vigorous movement and a partial mixing of the liquid. When the exchange is perfect, the vapors must acquire the exact equilibrium composition with the liquid $y_{n-1} = f(x_n)$, and the oxygen content will be reduced by the amount $y_n - f(x_n)$. The liquid, too is changed in composition, as it runs down the surface of the column and reaches the bottom, by mixing with the liquid collected there. We can arrive at the changes in composition on the strength of the following energy and material balances. In the permanent state, the sum of: 1) all the added and removed amounts of gas, 2) all the entering and leaving amounts of oxygen, and 3) all the added and removed amounts of heat must be equal to each other. Therefore, if V_n and V_{n+1} are the total amounts of vapor above and below the bottom, v_n and v_{n+1} the corresponding amounts of liquid, i'_n and i'_{n+1} the heat contents of the liquid, i''_n and i''_{n+1} the corresponding heat contents of the vapor, the following relationships are valid:

$$v_n + v_{n+1} = v_{n-1} + v_n \qquad (13)$$

$$v_n \cdot y_n + v_{n+1} \cdot x_{n-1} = V_{n-1} \cdot y_{n-1} + v_n x_n \qquad (14)$$

$$V_n \cdot i''_n + v_{n-1} \cdot i''_{n+1} = V_{n+1} \cdot i''_{n+1} + v_n i''_n \qquad (15)$$

The heat content of the liquid i' depends on x, the heat content of the vapor i" on y. The relationship is not exactly known, and we shall assume, that the heat content is composed additively from the heat contents of the components, and the vapor is always present in the dry saturated state. Let

$$i' = x . i'_{O_2} + (1 - x)\, i'_{N_2} \qquad (16)$$

$$i'' = y \,.\, i''_{O_2} + (1-y)\, i''_{N_2} \qquad (17)$$

where i'_{O_2}, i''_{O_2}, i'_{N_2} and i''_{N_2} are the heat contents of pure O_2 and N_2 at their boiling points under the total pressure of the system P. Moreover, since $i''_{O_2} - i'_{O_2} = r_{O_2}$ and $i''_{N_2} - i'_{N_2} = r_{N_2}$ represent the heat of vaporization of the pure components at the pressure P, we may replace equation 17 by

$$i'' = y\,(i'_{O_2} + r_{O_2}) + (1 - y)\,(i'_{N_2} + r_{N_2}) \qquad (17a).$$

Substitution of this equation into (15), and under consideration of (13) and (14),

$$V_n\,((r_{N_2} + y_n)\,(r_{O_2} - r_{N_2})) = V_{n+1}\,((r_{N_2} + y_{n+1})\,(r_{O_2} - r_{N_2})) \qquad (18)$$

$y_{n+1} < y_n$, and $r_{O_2} > r_{N_2}$, and this equation means that during rectification of the oxygen - nitrogen mixture the amount of vapors increase towards the top. Equations (13), (14) and (18) permit to determine the required oxygen content x_{n+1} of the liquid on the plate by elimination from them of V_{n+1} and v_{n+1}.

However, the effect of the variation of r_{N_2} and r_{O_2} on the rectification is very slight, as proven by the computations made, and we may assume in many cases that $r_{O_2} - r_{N_2} = 0$. We then get from the equation (18)

$$V_n = V_{n+1},$$

and therefore, from equation (13)

$$v_n = v_{n+1},$$

i.e. that the amounts of liquid and vapor remain unchanged along the whole of the rectification column, because the same considerations apply to all rectifier plates. We get, by substitution in equation (14)

$$x_n - x_{n+1} = \frac{V_n}{v_n} (y_n - y_{n+1}) \qquad (19)$$

This equation permits the continuous determination of the composition of the liquid and the vapors on the plate, by setting $y_{n+1} = f(x_n)$.

The equalization is not perfect on the actual plates, and y_{n+1} is always $> f(x_n)$. The ratio of the actual changes in composition of t vapors $y_n - y_{n+1}$ to the theoretical $y_n - f(x_n)$ will be called the efficiency of the plate. This efficiency depends primarily on the construction of the rectifier plate and varies as a rule between 0.4 and 0.8. When η is known, equation (19) may also be applied to actual plates, and y_{n+1} can be calculated from

$$y_{n-1} = y_n + \eta (y_n - f(x_n)) \qquad (20)$$

Should we assume, as heretofore, and as is also always justified in practice, that the vapor becomes poorer in oxygen through contact with the liquid, so that $y_n > y_{n+1}$, then, according to (19), x_n is also $> x_{n+1}$, that is, as the steam rises through the rectifier bottom, it always meets a liquid of lower oxygen content. The countercurrent flow of the liquid and of the vapors result in a more or less perfect equalization at the plate, the equilibrium of the vapors becomes again upset at the next plate, where it again becomes re-established, etc, and the rectification will present a continuous alternation of equilibrium upsets and re-formation. The sum of all these small adjustments results in such a change in composition, that the liquid very poor in oxygen at the top leaves the bottom of the column as almost pure oxygen, and conversely, the vapors which enter from below as almost pure oxygen, leave on top as nitrogen contaminated with very little oxygen.

The purity of the nitrogen escaping above depends, in addition to the nature and number of the rectification column plates, also upon the composition of the liquid entering from above. The vapors escaping above can not contain less oxygen, than corresponds to the equilibrium composition of that liquid. If the liquid air enters on top with 20.9% O_2, then the escaping vapors must contain at least 7% O_2, according to fig. 11. On the other hand, there is practically no limit for the purity of the oxygen produced if the vapors entering from below are produced by re-evaporation of the liquid in the column, because the vapors then always contain more oxygen then corresponds to the equilibrium conditions of the liquid drained. With the arrangement shown in Fig. 16, the oxygen-rich liquid on the bottom of the column is vaporized by the air to be separated, is liquefied under pressure in the counter-current exchanger inside the coil "a" placed in the liquid, and is returned at the upper end of the column after expansion in the valve "b". About 1/3 of the product is removed from the oxygen-rich vapors at the bottom of the column, while the rest rises through the column. In addition to the disadvantage that this single column unit does not produce pure nitrogen, only 2/3 of the oxygen in the air is separated in the pure form, because 1/3 remains with the nitrogen.

The vapors escaping above can only be composed of pure nitrogen, if the liquid supplied from above consists of pure nitrogen. This can be accomplished by the DRP 203,814 by installing two rectification columns in series, of which the first, under about 5 atm. pressure, produces only a preliminary separation of air into liquid nitrogen and a liquid containing 30 - 40% oxygen. The final separation into the pure compounds is done in the second column, under a slight excess pressure only, and is located above the pre-separation column. The difference in pressure in the two columns is intended to raise the liquefaction temperature of the nitrogen, entering the pre-separation column in the gaseous state, so that it could be condensed by giving up heat to the liquid oxygen descending in the second column. Theoretically, a pressure of 3.5 atm. is sufficient for the purpose; in practice, a somewhat higher pressure is required to have sufficient temperature difference for the heat exchange between the nitrogen, which is being condensed, and the evaporating oxygen.

The following phenomena occur in such a two column unit, shown in fig. 17; the compressed air, cooled to the saturation temperature in the heat exchanger is luquefied in a coil underneath the pressure column "a", and after expansion in the valve "b" to about 5 atm. is introduced at "c" in the middle of the column. The liquid flows down first over the plates in the bottom part of the column and most of it is then vaporized in the vaporization vessel placed underneath and gives up heat to the air condensed in "a". When rising again in the column, the vapors give up their oxygen to the liquid which trickles down, and becomes more enriched in nitrogen, than the liquid air introduced at "c". The vapors are next liquefied at the head of the column in the condenser "d". About half of the liquid so produced is returned to the pressure column to further free the rising vapors of their oxygen, so that the vapors and the liquid obtained from them will have in the final state only about 0.5 to 3% oxygen. The other half of that liquid is expanded through the valve "e" and returned to the head of the other column. A nearly equal amount of liquid to be vaporized, and containing 35 to 40% oxygen is taken from the bottom vaporization vessel and introduced into the middle of the upper column, where it combines with the liquid coming down, and enriched to approximately the same oxygen content. Finally, a liquid consisting of almost pure oxygen collects in the outer space of the condenser "d", is re-evaporated by the heat liberated in the liquefaction of nitrogen inside the condenser. Approximately

1/6 to 1/3 of these vapors are taken out at "f" as the final product, while the major portion rises again inside the column, and is drawn off finally at "g" as practically pure nitrogen. The cold contained in the withdrawn oxygen and nitrogen is carried over to the incoming air in counter-current heat exchangers.

PRODUCTION OF COLD DURING THE AIR SEPARATION.

Disregarding the heat losses, and assuming that all the separation products leave the columns in the liquid state, no cold production, in the sense of absorbing heat at the lower separation temperature from some refrigerant, and giving it up to cooling water at room temperature, will be required in the separation column, with the rectification proceeding under stabilized conditions. Conversely, cold must be continuously transferred from the higher temperature of the oxygen boiling in the bottom column to the lower temperature of the boiling nitrogen in the upper end of the column. Temperature differences are thus continuously produced, and the rectifying action of the column is based on their equalization. This transfer of cold to the upper end of the column corresponds to the action of a refrigerating machine operating between two very low temperatures. The energy required for it is supplied by the two column apparatus by the necessary compression of air to at least the pressure in the pre-separation column. On the other hand, the still higher compression, required to liquefy the air in the coil "a" is essentially avoided, if the air is transferred into the high pressure column at "f" in the form of vapor.

The energy for the compression of air to the pressure of the bottom column can be additionally reduced, if part of the air (theoretically 40% at most) is introduced in the vapor form directly into the middle of the upper column, using a process suggested by Lachmann. In this introduction of gaseous air, the amount of cold transferred from the bottom to the top end of the column would be reduced, and with that also the temperature differences inside the column to carry out rectification. The Lachmann process is but rarely used because of the difficulties it introduces into the rectification.

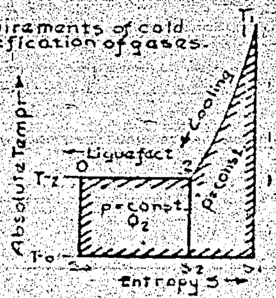
When stabilized conditions have been reached, the transfer of cold to the upper end of the column involves no new production of cold, and an amount of cold once produced, given up by the condensing oxygen during the rectification of nitrogen, is continuously transferred to the liquid nitrogen. The production of addiational cold becomes necessary only when part of the separation products is removed in the liquid state. In the great majority of cases, the products of separation are needed in form of a gas at atmospheric pressure. Nor do the counter-current exchangers use up any cold when the heat exchange is perfect and losses of cold are prevented, and the whole separation unit requires no additional production of cold when the conditions have become stabilized and the separation process is carried out with no losses. On could even continuously remove in a special unit an additional amount of cold produced during the throttling of the pressure of the pre-separator, and which amounts to 0.3 kcal/m^3 with no precooling, and to 0.5 kcal/m^3 with precooling to -50°.

These considerations should make it clear, that in normal separation installations, where the products of separatinn are obtained in the gaseous form, the total additional cold is required merely to compensate for the unavoidable losses of cold, in contradiction to liquefaction installations, in which only a part of the cold produced is used to cover up losses of cold. These losses of cold are a result of the imperfect insulation and of the losses in heat exchange of the counter-current exchangers, as has already been shown during the discussion of the air liquefaction installations. They amount to 2 to 4 kcal/m^3 of air used. The cold produced by the throttling-down of the pre-separation column to atmospheric pressure is not sufficient to cover these losses, and an additional amount of cold must be produced, by compressing either all of the air, or a part of it, to a higher pressure than 5 atm. The air compressed to higher pressures becomes liquefied before the intake into the coil "a", fig. 17, while the air compressed to only 5 atm. enters the pressure column in the form of vapor.

In fig. 18, the required pressure with pre-cooling to -30°C as well as the total compression work per m^3 of air is presented as a function of the fraction of the air under higher compression, for the two cases mentioned, when the additional cold required equals 2 and 4 kcal/m^3 of air. The drawing shows that the energy requirements for the actual separation with a given expenditure of cold can be markedly reduced by decreasing the amount of the more highly compressed air, in spite of the higher pressure then required. The frequent industrial practice of separating the total air into "high pressure air" and "low pressure air" results therefore in a marked saving in energy for compression, compared with the case when all of the air (100% high-compression air, fig. 18) is compressed to the same high pressure. The upper branch of the curves in Fig. 18, drawn in broken lines, is obtained when there is a possibility of obtaining the same relative amounts by using two different pressures. The higher of the two pressures will however require a greater consumption of energy, and does not therefore enter into consideration.

The high pressure circuit is very effective for liquefaction of air, is but little suited for the production of cold during rectification, because nearly all of the air must be made to participate in the separation, and must therefore be completely expanded. On the other hand, the high pressure circuit can be successfully used, wherever the separation is produced wholly or in part by a partial condensation, e.g. in the separation of water gas and of coke oven gas.

Fig. 1. Requirements of cold for the liquefication of gases.



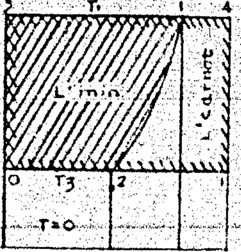
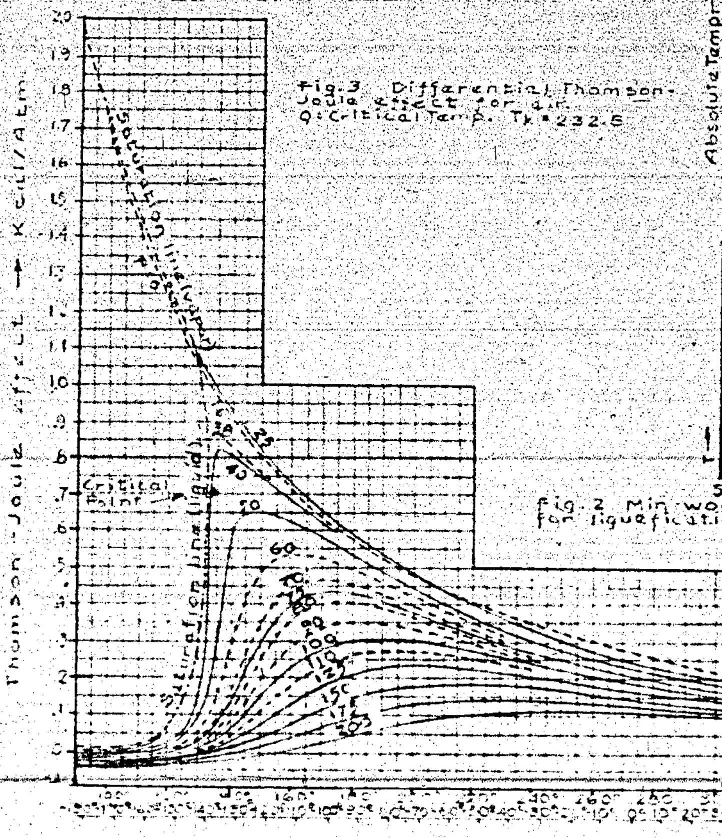


Fig. 2 Min. work requirements for liquefication of gases.

Fig. 3 Differential Thomson-Joule effect for air.
Q: Critical Temp. Tk = 232.5



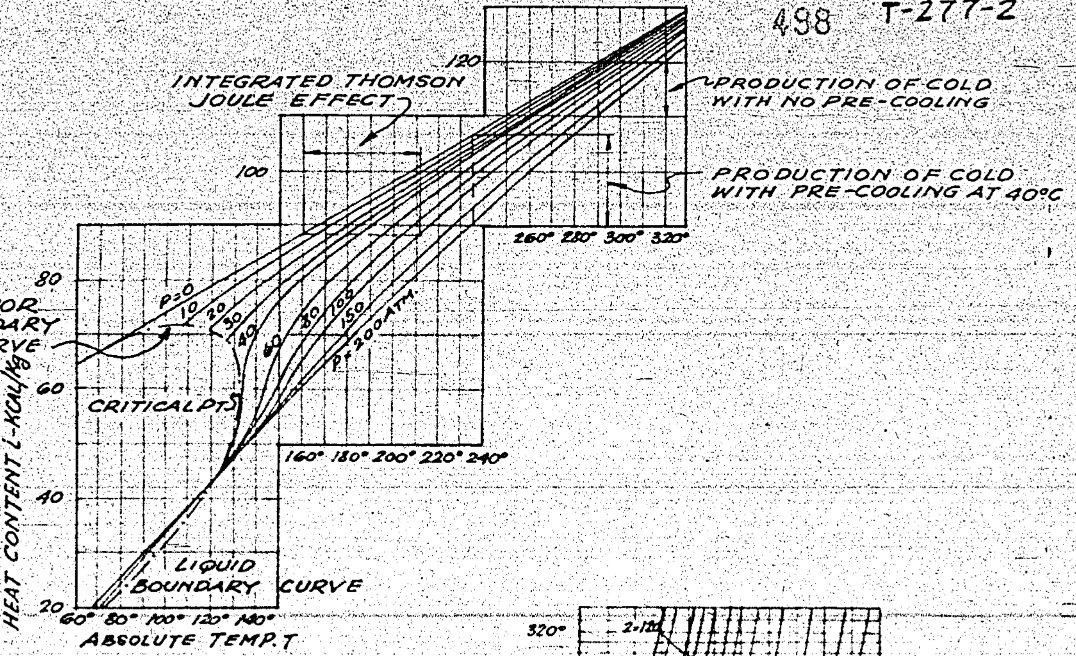


FIG. 4 i, T DIAGRAM

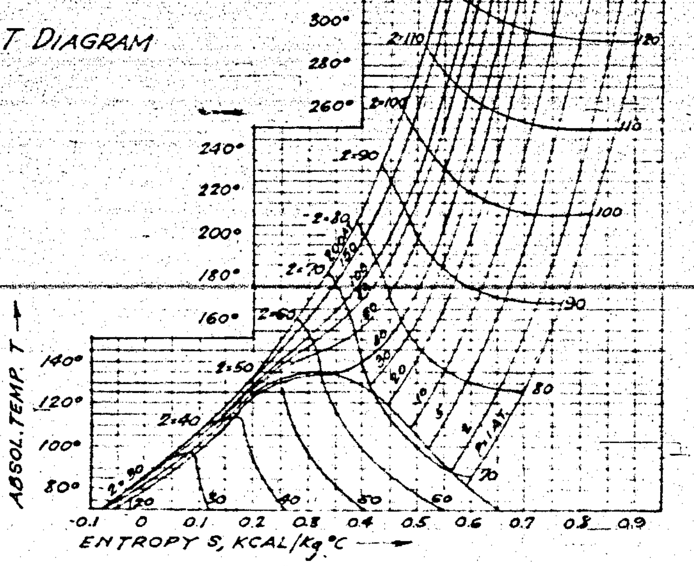


FIG. 5, T,s DIAGRAM

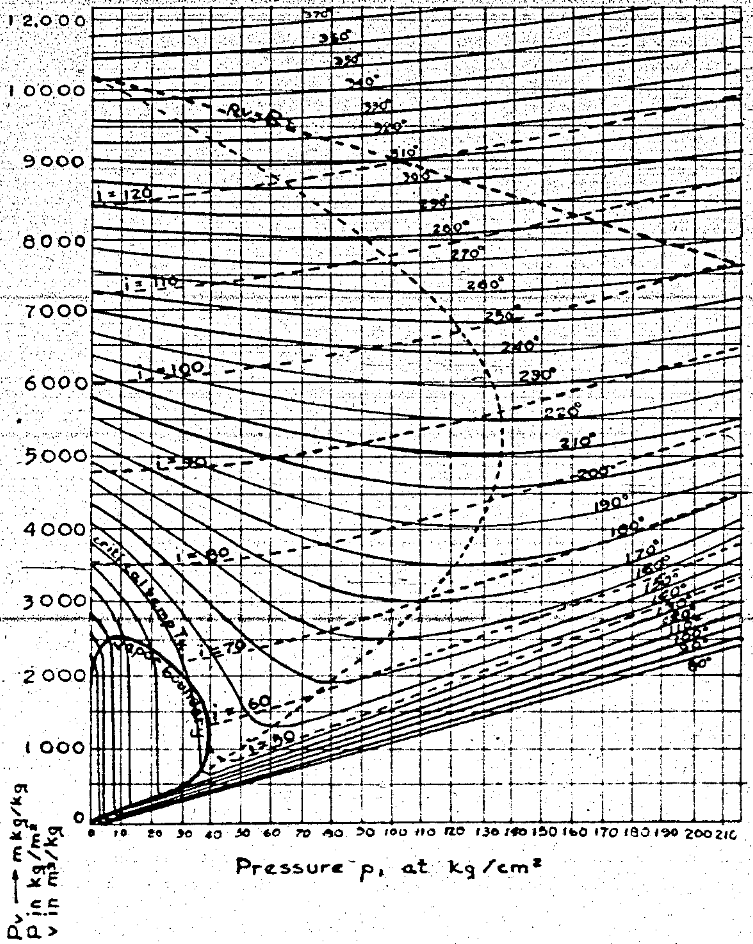


Fig. 6. Pv, p diagram for 1kg. air.

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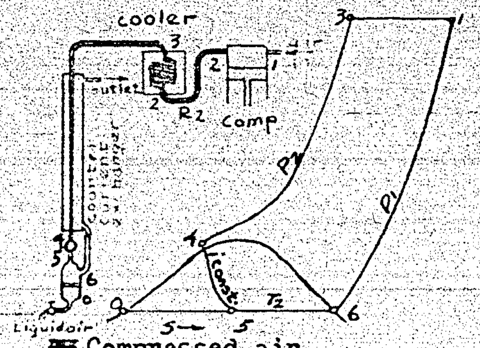
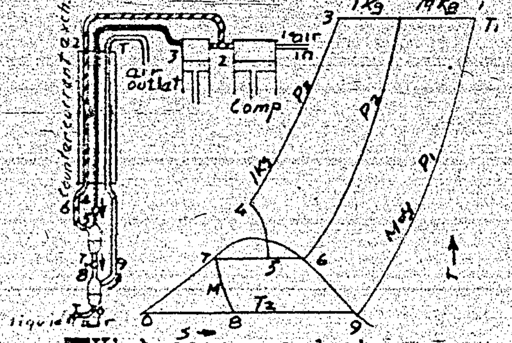


▬ Compressed air
= Exhaust air
Fig. 7a - 7b. Linde air liquefacation with simple exhaust(scheme & diag.)



▬ High compressed air
= Interm. comp. air
= Exhaust air.
Fig. 8a-8b. Linde air liquefaction with high pressure circut.(scheme & T s diagram)

1

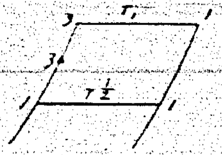
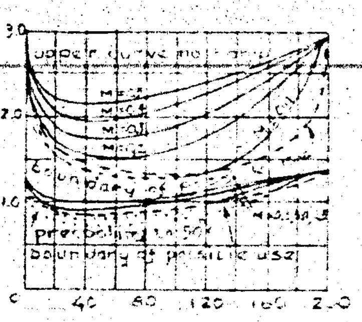
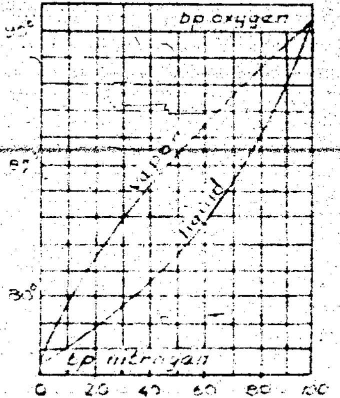


Fig. 9. Liquefication of air with precooling. (Computation of output of refrigerator.)





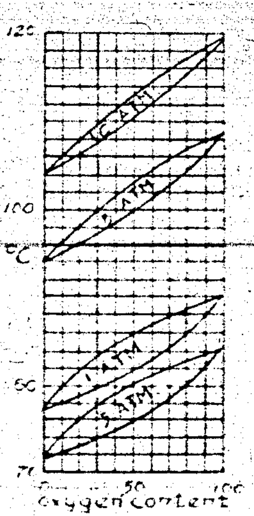
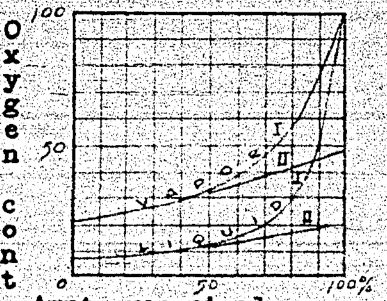


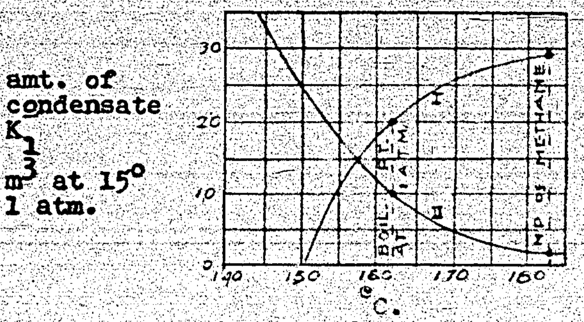
Fig. 10. Liquefaction of air with high pressure circut. Energy per 1 kg Liquid air. Losses not considered.

Fig. 11. Equilibrium of boiling oxygen-nitrogen mixtures at 760m.m. Hg.

Fig. 12. Equilibrium comp. of boiling oxygen-nitrogen mixtures at different pressures.



.. Amnt. vaporized
I Vapor produced escapes immediately (fractionating vaporization)
II Total vapor remains in contact with liquid.
Fig 13. Vaporization of liquid air.



I Amt. of condensate from $100 m^3$ mixture.
II Saturation pressure P_1 of methane.
Fig. 14.

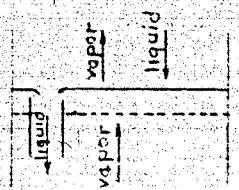


Fig. 15. Rectifier plate.

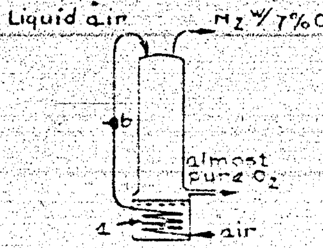


Fig. 16. Single column apparatus.

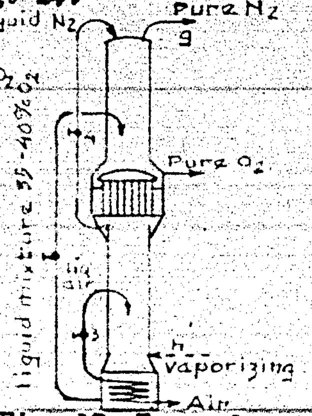


Fig. 17. Two column apparatus.

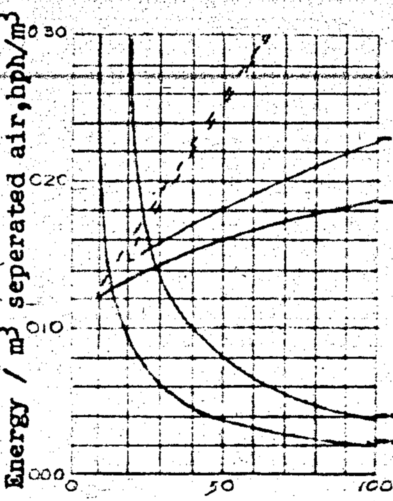


Fig. 18. Division into high and low compr. air with precooling to -50°C.

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

COAL REFINING PROCESS

(Patent Application by Pfirrmann)
Ludwigshafen, 27 Jan. 1942

It is known that solid coal substances, like bituminous or brown coal, etc., can largely be converted into non-liquid soluble or meltable bitumen under hydrogenation conditions, i.e., at temperatures between 400°-500°C. and at elevated pressure, in the presence of largely aromatic or hydro-aromatic hydro-carbons, if less H_2 is used than is required to convert the coal into liquid hydro-carbons, or if the coal is treated, without the addition of H_2 , with hydro-carbons, such as tetraline, which can give off H_2 at hydrogenation temperatures.

From the converted products, which can also be freed of ash by filtration, the pasting oil is again recovered by distillation and is recycled. In order to facilitate this recovery, mostly lighter boiling hydro-carbons are used for pasting, e.g., light oils from 140°-220°C. or middle oils from 200°-300°C. on, or the boiling temperature of higher boiling oils is reduced by vacuum or steam distillation, so that there still remains a gap between the boiling end of the pasting oil and the beginning of distillation or decomposition of the recovered bitumen.

The bituminous product produced is similar to natural bitumen or distillation residues in its range of use. Among others, it can also be carbonized at low temperature (verschwelt), in which operation it may yield up to 60% tar, depending upon the kind of coal and the hydrogen consumption. It is further suitable as a binder for briquetting, carbonization, or coking of poor or non-caking(backend) coal or coke breeze, whereby the entire tar constituent is recovered from the bitumen.

The thorough mixing of the bitumen with the coal to be caked or the coke breeze, as well as the manufacture of the pressed products, is facilitated and improved, if the softening point of the bitumen is not above 120°C., properly only about 50-90°C. To be sure, such a bitumen can be obtained directly from the coal by longer residence time and somewhat higher H_2 consumption. But for better utilization of the high pressure apparatus it is more profitable to work with lower residence times and correspondingly higher temperatures and pressures, e.g., above 450°C. and 600 atm., i.e., with increased thruput, whereby some bitumina with higher softening points are obtained. To make the bitumina better suitable for briquetting, enough oil is added until the softening point, say 70°C., is reached, or a part of the oil used for pasting the coal, e.g. 10-20%, is left in the bitumen from the start, whereby the desired softening point is also obtained.

If, e.g. the coal is pasted with an aromatic middle oil boiling between 200-300°C. in the proportion of 1:1 and H_2 is supplied at the rate of $0.5 m^3$/kg coal at 460°C. and 600 atm., with a coal thruput of 1-1.5, roughly 10-15% of the middle oil used must be left in the bitumen obtained in order to lower the softening point, which is about 110°C. in the oil-free bitumen, to 75°C. If we work without H_2 with a middle oil containing tetraline and homologues supplying H_2, softening points around 200°C. and above are obtained in the oil-free bitumen, even with reduced thruputs. In this case, up to 40% oil must be added or a corresponding amount left in the pasting oil in distillation. The oil constituents in the bitumen must be kept still higher if coal, rich in bitumen, is heated under pressure or extracted only with higher boiling, aromatic hydro-carbons, to obtain a briquette binder.

This oil constituent is first removed from the recycle oil in the recovery of the bitumen, but reappears in the L.T.C. tar in the carbonization and coking of the briquettes, at least where distillable oils are concerned, here, however, mixed with the tar produced from the coal and bitumen by decomposition. It is no longer possible to separate it from the tar by distillation, and, in order to cover the loss, we are forced to recycle a mixture of the original pasting oil with the L.T.C. tar distillate, because a constant supply of make-up oil is not possible, since it would make the whole process impossible. It was shown in the continuous replenishment of such an oil that the oil fractions distilled from the L.T.C. tar are no longer good solvents for the coal substance and that considerable losses occur in the high pressure section, so that the coal conversion and consequent yield of bitumen is constantly reduced in continuous operation. The cause of such unfavorable behavior may be the presence of paraffinic hydrocarbons, which may be present when young coal and brown coals are used in considerable proportions. At present it is due to unsaturated hydrocarbons and oil resins, which condensate and polymerize together with the coal substance, or form coke, so that the pasting oil losses are particularly heavy when working without hydrogen.

The filtrability also deteriorates, which causes considerable difficulty in the production of ash-free bitumen and electrode coke.

It has now been discovered that a pasting oil suitable for the production of bitumen may be obtained continuously in sufficient quantity, if the tar obtained in the carbonization (schwelen=L.T.C.) of coals or briquettes mixed with bitumen is not decomposed in normal distillation, but is subjected to pressure distillation, in which the bituminous and high molecular constituents, up to coke, are split up.

Example

Properly, the tar is first filtered to reduce the ash content, though not very high, still further. This is easy. The tar, still containing about 0.1-0.15% ash, is then pumped into a pressure vessel, not heated but well insulated, at 3-25 atm. thru a tube heater, which heats it up to 450-525°C. At the same time the residual heat required for decomposition is supplied by an auxiliary gas preheated to 450-600°C., such as the L.T.C. gas in the circulating system proper, or nitrogen, hydrogen, or steam. The distillable oils at hand, as well as the oil vapors rich in aromatics, produced by splitting from the high molecular hydrocarbons and the tar bitumina, are carried off with the flushing gases and condensed under pressure. The rest is a fairly dense, hard and ash-poor residue, resembling coke, suitable for metallurgical purposes, particularly as electrode coke in the manufacture of aluminum, after it has been freed of its volatile constituents and made conductive by heating without pressure to temperatures above 850°C.

The yields in coke residue and pressure distillate vary somewhat, depending upon the kind of coal, the carbonization system, and the binder. If, e.g. the L.T.C. tar is produced in a flushing gas kiln from poor caking bituminous coal rich in gas, with more than 35% volatile constituents, and a binder consisting of 12% of a hydrogenation bitumen produced by incomplete hydrogenation of a coal pasted with an aromatic middle oil and still containing 15% pasting oil, is used for the briquettes charged, about 60% of the tar originates from the coal and about 40% from the bitumen containing pasting oil. If this tar is distilled under a pressure of 10 atm. at 490-520°C. with the aid of H_2, the largely aromatic distillates present are recovered almost entirely. The high molecular and paraffinic hydrocarbons, the oil resins and unsaturated, and the humic acids, are prevented from being distilled off by the pressure and are split up by forming easily distillable, stable, H_2-poor hydrocarbons, which also contain phenols, and a splitting residue resembling coke, which accumulates in the splitting chamber operating intermittently.

From 100 parts of the charged, filtered flushing gas tar, with a pour point (Stockpunkt) of-270°C., an asphalt content of 8.8%, and a middle oil constituent of 16.8% (distilling up to 300°C.), the following yields were obtained:

64.5% pressure L.T.C. oil, suitable for fuel oil,
with a pour point of -8°C. and a spec.
gravity of 1.042 @ 20°C.
29.0% coke residue containing 0.45% ash, 6.5% gas loss.

The pressure L.T.C. oil had a middle oil content (-300°C.) of 45.3%. Based on the charged tar, there was, therefore, a middle oil yield of 29.2%, or almost twice as much as was present in the original L.T.C. tar. This middle oil contains much aromatics, as well as low phenols, and is very satisfactory for pasting the coal for the production of bitumen. Other products are a stable fuel oil suitable for storage and easily miscible, with a pour point and specific gravity such that it will not sink even in ocean water, and an ash-poor coke, which, after calcining (glühen) at 900-1150°C. for a short time, can be used as high grade electrode coke. An additional 2-3% of aromatic tar is obtained in this calcining process. If the coal is carbonized in whole or in part before briquetting, the tar obtained can also be pressure distilled.

If the coal or coke is bound to a hydrogenation bitumen by a coal extract produced from pulverized bituminous coal in a higher boiling aromatic oil by heating under pressure to 300-400°C., 25-35 parts of coal are required to 75-65 parts of the aromatic oil for a softening point of 60-80°C. If 15 parts of the bitumen so produced is used for briquetting 85 parts of poor caking coal, 9.75-11.25 parts of L.T.C. oil to 100 parts briquettes must be obtained from the added oil and the binder oil alone, or more than from the coal itself. If this oil were to be taken from an outside source every time, the whole process would fail because of it. However, it was found that the oil obtained in pressure distillation and splitting was also much better suited for this extraction of the coal than the L.T.C. tar proper, so that it is possible not only to complete the oil circulating system for the binder recovery with this pressure L.T.C. oil, but, in addition, to utilize 50-60%, based on the tar obtained from the coal alone, in the form of a stable fuel oil. The coke-like residue is subjected to a calcining process and then represents an ash-poor electrode coke equal to about 25-30% of the L.T.C. tar originating from the coal.

The possibility to recover high grade electrode coke from the unstable and low value constituents of the L.T.C. tar must also be considered a great advantage of the process at hand. Electrode coke for aluminum recovery must not contain over 0.6% ash. The bituminous products suitable for making electrode coke must, therefore, be carefully filtered so that the coke, which represents only a fraction of the original filtrate, is not inadmissibly enriched with ash. This filtration is satisfactory only with products which are produced by incomplete hydrogenation with middle oil pasting and H_2 deficiency or with oils giving off H_2. Products of the non-hydrogenating fraction can only be separated very coarsely from the insoluble constituents by precipitation or centrifuging. Fine filtration, as required for electrode coke manufacture, is practically impossible with pressure extracts. On the contrary, it was found that the L.T.C. tar obtained could be readily fine filtered, so that electrode coke can now also be obtained by means of the above combination by the simple pressure extraction of coal.

In summary, the process consists of producing usable pasting oils by pressure distillation (Druckverschwelung) of filtered L.T.C. tars, up to coke, for the recovery of bituminous binders by incomplete hydrogenation and/or extraction of coals, with or without H_2, wherein a part of the pasting oil is left in the bitumen obtained and/or fresh oil is added to obtain a binder with low softening point particularly suitable for briquetting. In the carbonization (verschwelen) of the coal mixed with this binder the oil originating from the bitumen mixed with the tar originating from the coal is largely recovered, but cannot be separated from it, and is, therefore, unsatisfactory for renewed coal pasting. On the contrary, the oils obtained by pressure distillation of the L.T.C. tar are well suited for renewed pasting of coal. This step makes it possible to complete the recycle process fully and to cover the losses in pasting oil too. By-products of pressure distillation are a stable fuel oil and high grade, ash-poor electrode coke.

Patent Claims

Process for producing solid coke or coke briquettes, fuel oil, and electrode coke from poorly or non-caking coal, or coke breeze with a bituminous binder, produced by incomplete hydrogenation or extraction of coal by means of recycled H_2-poor hydrocarbons, characterized by subjecting the L.T.C. tar obtained in the carbonization (schwelung) or coking of coal mixed with a binding medium or of compressed coke breeze, possibly after previous filtration, to a decomposing pressure distillation, for the manufacture and continuous replenishment of the extraction medium, whereby the distillate constituents originating from the L.T.C. tar are used like the oils added to the binding medium for adjusting the softening point so that they can be recycled for the recovery of the bitumen, while the excess pressure distillate can be used as fuel oil and the residue as electrode coke.

C H. Patents

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T-279
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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR PRODUCING OIL FROM COAL

German Patent 720824
Class 12$_o$, Group 1o$_5$
18 Aug. 1936

Issued to
I.G.Farbenindustrie, A.G.
Frankfurt A.M.

By
Dr. Mathias Pier, Heidelberg, and
Dr. Walter Krönig, Ludwigshafen/Rh.

DRP 720824

In splitting pressure hydrogenation of oils in the vapor phase, it is customary to use fixed catalysts in the reaction vessel. It has also been tried to use catalysts in a similar manner in the pressure hydrogenation of coal-oil mixtures, by passing the mixture thru the reaction space from the bottom towards the top at temperatures above 370° C., with the catalysts, e.g. in the form of metal plates, arranged in a fixed position in the reaction space. It was shown thereby, however, that the catalyst is rapidly soiled by depositions, becomes ineffective and clogs the reaction space in a short time.

It was now discovered that the life of a fixed catalyst in the pressure hydrogenation of coal pasted with oil, particularly of brown coal, is comparatively long, if the reaction temperature is held below about 415° C., preferably within the range of 330 to 400° C., and the coal-oil mixture is passed thru an upright reaction vessel from the top towards the bottom. The H_2 pressure herein may be between 100 and 500 atm.

With this operating method the asphalts are not converted into asphalts poorer in H_2. Consequently, no products of condensation harmful to the catalyst are formed, so that large quantities of coal paste can be processed without changing the catalyst. Thus, considerably smaller quantities of catalysts need be used than with finely distributed catalysts.

In spite of its high content of solid matter, the coal paste can be passed thru the reaction space, in which the catalyst is arranged in a fixed position, without appreciable difficulty. The effectiveness of the catalyst in this procedure is affected neither by the coal paste nor by high molecular products of depolymerization formed therefrom.

The coal is used in finely pulverized form and mixed with an oil boiling above 200° C., possibly even above 325° C., and which is free of or poor in asphalt. An oil originating from the same coal is excellently suited. As a rule, so much oil is added to the coal that the final mixture contains about 10 to 50% coal. If it is desired to obtain a low asphalt concentration (up to 20%) in the heavy oil to be recovered, appreciable quantities of gaseous and low boiling liquid hydrocarbons are formed in the usual pressure hydrogenation of coal. On the other hand few split products, e.g. less than 8% gaseous hydrocarbons and less than 20% liquid products boiling below 300° C. are formed from the water-and-ash-free coal under the above conditions of reaction.

Preferred catalysts are compounds of metals, particularly the oxides and sulfides of metals of the 5th and 6th groups of the periodic system in the form of pieces, as e.g. regularly formed shapes, such as pills or Raschig rings, properly such of more than 3 mm diameter. Their size depends upon the size of the reaction space. They are arranged so that the coal-oil mixture must pass between them in comparatively narrow intermediate spaces. Care must be taken, e.g. by the use of stream lined shapes, that not too much resistance is offered to the flow of the incoming material, because the catalytic substance may otherwise be rubbed off by the inorganic constituents of the coal. In order to provide suitable spaces for the flow of the reaction material, shapes of different sizes are used or they are staggered. The largest possible catalyst surface must be provided, but still allow sufficiently large spaces between the catalyst shapes to permit the passage of the ash.

Besides the fixed catalysts, volatile substances, such as halogens or metalloid halogenides, e.g. organic halogen compounds or volatile sulfur compounds, may be added, or the coal itself may be drenched with a solution of a catalytically acting substance, such as the watery solution of a salt of a catalytically effective metal, or finely pulverized catalysts may be mixed with the coal. The coal may also be treated with acid before use to neutralize the ash.

The hydrogen is fed either in co-or counter-current thru the reaction vessel, but preferably co-current in the preheater, at least part way.

It is also essential to avoid a mixture of the primary products of depolymerization formed at the beginning of the reaction with the products formed toward the end of the reaction. This is achieved by a suitable division of the reaction space, such as using several reaction vessels in series, connected with each other by one or more pipe lines or overflow devices. Pumps or other devices facilitating the conveying of the reaction material may be built into the lines conveying the higher boiling products containing solids.

If operations are conducted in the prescribed manner, only little splitting of the high boiling substances primarily formed from the coal occurs. In case these still contain asphalts or resins, they can again be treated in the same way as the starting materials after separating the ash.

The reaction materials can, in this case, flow thru the reaction space from bottom to top, and the catalyst may be arranged denser and possibly irregular.

Example

Central German brown coal is pasted with brown coal L.T.C. tar in the proportion 40:60, after its basic constituents have been neutralized with sulfuric acid, and, together with hydrogen @ 250 atm., after preheating to 355° C. is passed thru a reaction space filled with alternate layers of solid cylinders 10 mm diameter and hollow cylinders 15 mm outside diameter, consisting of an equi-molecular mixture of molybdic acid, zinc oxide and magnesia, which has previously been treated with H_2S @ 400° C. and 10 atm. The organic matter in the coal is thereby converted to the extent of 78%. The oil recovered has the following composition:

13	parts/wt.	gasoline
43	" "	middle oil
15	" "	paraffin
25	" "	lubricating oil
4	" "	asphalt

With this operating method, operations may continue undisturbed for weeks. If on the contrary, the coal paste is passed thru the reaction space from bottom to top, as has been customary to date, the reaction space is clogged within three days to such an extent that operations must be interrupted.

Also, if the coal paste is passed thru the reaction space from top to bottom at say 470° C., instead of 355° C. at otherwise customary pressure hydrogenation temperatures, and other conditions being equal, continuous operation is impossible, because the reaction space will be fouled after only two days.

Patent Claims

1. Process for producing high boiling oils, particularly lubricating oils, by pressure hydrogenation of coal mixed with oils free of or poor in asphalt, in the presence of fixedly arranged catalysts in the form of pieces, at temperatures below 415° C., characterized by passing the coal-oil mixture from top to bottom thru an upright reaction vessel at temperatures from 330 to, preferably, 400° C.

2. Process according to Claim 1, characterized by using coal drenched with a solution of a catalyst or mixed with a finely pulverized catalyst.

C.H. Patents

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR THE PRESSURE HYDROGENATION OF SOLIDS FUELS

German Patent 720825
Class 12o, Group 1o5
10 Jan. 1937

Issued to
I. G. Farbenindustrie, A. G.
Frankfurt A. M.

By

Dr. Mathias Pier, Heidelberg, and
Dr. Walter Krönig, Ludwigshafen/Rh.

DRP. 720825

In the pressure hydrogenation of solid fuels, particularly of coals, it is customary to paste this with oil fractions, particularly middle oils, or heavy oils, or mixtures originating in hydrogenation.

It has now been discovered that mixtures of light, medium and heavy hydrocarbon oils, like gasoline, diesel oils, lubricating oils, and particularly fuel oils, can be produced to advantage by the pressure hydrogenation of solid fuels, e.g. bituminous coal, brown coal, oil shale or peat, if products of hydrogenation, consisting of middle oils, heavy oils, as well as asphaltic or solid residues, are used for pasting the starting material for the subsequent pressure hydrogenation. That part of the products of hydrogenation used for pasting, which has been freed only of gasoline, therefore, still contains substances, which have not been liquefied or converted, as well as ash and possibly solid catalyst. Surprisingly, the recycled asphalts and ash cause no disturbances in the hydrogenation of coal. The hydrogenation of coal is greatly simplified by the above invention, since it makes a special processing of the letdown to pasting oil as, for instance by carbonization, unnecessary.

The pressure hydrogenation of solid substances is properly done at temperatures between 350 and 550° C. The temperature may be increased gradually or in stages during the reaction. For example, several reactors with rising temperatures may be arranged in series. Pressure hydrogenation may be conducted with more or less hydrogen, even with so little that only about 2 to 4% H_2, based on the dry, ash-free feed, is absorbed.

The pressures employed are, as usual, about 50 atm. or more, as for example, 300 to 700 atm. The thruput is 0.4 kg of solid feed per liter reaction space per hour, or more.

The catalysts known to pressure hydrogenation are properly used, as, e.g. the metals of the 5th to the 8th groups of the periodic system or their compounds, particularly their sulfides or oxides, in given cases together with halogen or metalloid halogenides, such as organic halogen compounds. Tin and its compounds have also proven to be good catalysts. The use of carriers, such as brown coal Grudecoke, is advantageous in many cases.

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The separation of the gasoline from the products of hydrogenation used for pasting is accomplished by removing the residue (Abschlamm-letdown), consisting of solids and higher boiling constituents, from the bottom of the hot catchpot, in which all the gaseous, vaporous, liquid and solid products of reaction are collected, while the gasoline, together with the H_2 and part of the middle and heavy oil pass off at the top as gases or vapors. These substances are then separated from the H_2 by condensation, the gasoline is distilled off the condensate, and the residual middle and heavy oil again added in whole or in part to the residue (letdown) drawn from the hot catchpot in liquid form. Part of the residue can also be returned to the reaction space without previous dilution with middle and heavy oil, either still hot or after reheating.

Part of the residue mixed with middle and heavy oil is used directly for pasting new feed material without separating the solids. The other portion, not required for pasting, is freed of its solids by centrifuging or filtration and used directly as fuel oil, or further hydrogenated to gasoline or diesel oil, or advantageously slightly enriched with H_2 for superior fuel oil, or used for some other purpose.

To be sure, a pressure hydrogenation process, in which coal paste is drawn from the hydrogenation zone and returned to the preheater after adding fresh coal paste, is already known. However, this operation is not for pasting the coal, but for increasing the concentration of the catalyst in the preheater. Above all, pasting in this case is not done with products drawn off before completion of the reaction, but with finished products of reaction, which contain solids.

Example

Bituminous coal is pasted with an equal quantity of a mixture of 35% middle and 65% heavy oil and solids (see below) recovered in pressure hydrogenation and hydrogenated under a pressure of 600 atm. and a temperature of 475° C. in the presence of 0.06% tin oxalate and 1.15% ammonium chloride, based on the coal. The thruput equals 0.5 kg coal per liter reaction space per hour. In this process, 73 parts of oil are newly formed for 100 parts of coal charged. Gasoline, middle oil and part of the heavy oil, together with the hydrogen, are drawn in vapor form from a catchpot held at 460° C. and connected to the reaction vessel. The hydrocarbons are condensed, the gasoline boiling to 215° C. (12% based on the coal charged) is distilled off and the residual, consisting of middle and heavy oil, is mixed with the residue (letdown) drawn in liquid form from the hot catchpot and containing ash, high boiling constituents and unconverted coal as well as catalyst. Another portion of the letdown is recycled directly to the preheater and thus returned to the reaction vessel.

A part of the mixture, consisting of middle oil, heavy oil and residue, is used directly for pasting new coal without removing the solids. The other part, containing 61% oil, based on the coal charged, is freed of ash, unconverted coal and catalyst by centrifuging. The oil is hydrogenated under a pressure of 600 atm. at a temperature of 470° C. with 1% of finely distributed catalyst, consisting of molybdic acid or brown coal Grude (coke) in such a manner that the asphalts are reduced. This operation yields a stable fuel oil, which can be readily pumped and causes no trouble in valves or nozzles.

Patent Claim

Process for the pressure hydrogenation of solid fuels, such as bituminous coal, brown coal, oil shale, or peat, using a portion of the products of hydrogenation for pasting the feed materials, characterized by using hydrogenation products, consisting of middle and heavy oils as well as asphaltic and solid residues, for pasting.

C.H. Patents

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR THE PRESSURE HYDROGENATION OF SOLID FUELS, SUCH AS COAL OR PEAT.

German Patent 720826
Class 12_o, Group 1_{05}
24 December 1937

Issued to
I. G. Farbenindustrie, A. G.
Frankfurt A. M.

By
Dr. Walter Krönig, Ludwigshafen/Rh.

DRP 720826

In the customary pressure hydrogenation of solid carbonaceous fuels, products are often obtained from which the solid constituents are difficult to remove by filtration or centrifuging.

It has now been discovered that readily filtrable products are obtained by pressure hydrogenation of solid carbonaceous fuels if gases free of or poor in H_2 are introduced during the process at one or more points behind the first third of the reaction space, at a temperature only slightly below the temperature in the reaction space, in such quantities that the H_2 partial pressure drops to about one-half or less.

To be sure, it is already known that, in order to avoid or eliminate an undesirable rise in temperature, gases may be introduced into the reaction space in pressure hydrogenation, at a temperature below that in the reaction space under such conditions that cooling follows. However, special care has been taken herein not to reduce the hydrogenation gas so much that the H_2 partial pressure will drop below about 75%.

On the contrary, this invention does not attempt to regulate the temperature. Rather, in order to gain the above named different objective, it is necessary to reduce the H_2 partial pressure more than in the known operating method after an appreciable hydrogenation has taken place.

The operation is performed so that the crushed feed materials, e.g. bituminous coal, brown coal, or peat, are pasted with an oil, such as heavy oil, or, better still, a middle oil, or with hydrogenated multi-grained hydrocarbons, or mixtures of these substances, in the proportion of, e.g. 1:1 or 1:2, and treated with H_2 or gases rich in H_2 at temperatures between about 300 and 500° C. and pressures between 50 and 1000 atm., particularly 200 to 600 atm., preferably in the presence of catalysts. About 700 to 4000 m^3 H_2, generally 1200 to 2500 m^3, are injected per ton of feed material, free of ash and water.

After partial hydrogenation has taken place, i.e. after the reaction material has passed thru more than 1/3, say 1/2, of the reaction space, a gas free of or poor in H_2, such as N_2, CO_2, steam or a portion of the hydrogenation gas coming off the reaction vessel, poor in H_2 and containing gaseous hydrocarbons, is conveyed into the reaction vessel thru pipes connected to the reaction vessel at these points, at a temperature only slightly below that in the reaction vessel, say about 50° C. It is herewith generally proper, but not absolutely necessary, that the total pressure be maintained in the reaction vessel. The H_2 partial pressure, which may equal 200 to 600 atm. in the first third of the reaction space, is reduced to about one-half and less, 30-70 atm., for example, by the addition of the gas mentioned. A small portion of the gas injected to reduce the H_2 partial pressure may also be introduced for temperature regulation at ordinary or only slightly higher temperature.

High boiling oils containing asphalt are principally obtained with this operating method. These can easily be freed of their solid constituents by filtration or centrifuging.

Example

Finely pulverized Rhenish brown coal is drenched with a 2% watery solution of ammonium sulfide and then pasted with a middle oil, boiling at 200 to 275° C. and obtained by pressure hydrogenation from the same coal, in the proportion of 1:1. One-half part by weight of the residue obtained in coal hydrogenation and 3% Luxmass to one part/weight of coal are also added to the paste. This mixture, together with 1000 m^3 of 98% H_2 per ton of pure coal, is heated to 425° C. at a pressure of 300 atm. in a gas-fired preheater and then conveyed into an enlarged reaction vessel. After it has passed thru about 2/5 of the reaction space, 1400 m^3/t pure coal of a gas containing 25% H_2 besides hydrocarbons, CO and CO_2 and obtained in the expansion of the product of reaction, is injected into it at a temperature of 410° C. The H_2 partial pressure in the reaction vessel is reduced to about one-half thereby. The product of reaction is then split in a catchpot kept at 410° C., whereby the vaporous products pass off with the H_2.

The coal is 95% converted. The oil recovered consists of 5% gasoline, 5% middle oil, and 90% of oils boiling above 275° C. After the portion required for pasting fresh coal has been separated from it, the middle oil is added to the high boiling reaction product separated in the catchpot and this is then filtered at 200° C. and 8 atm. pressure. A thruput of 700 kg/m^2 filter surface/h is obtained in this operation.

If a gas containing so much H_2 that the partial H_2 pressure in the reaction space is reduced to only about 75% is injected into the reaction space at the given point under otherwise equal conditions, a product is obtained which is more difficult to filter. The capacity of the filter then is only 150 kg/m^2/h.

Patent Claim

Process for the pressure hydrogenation of solid fuels, as coal or peat, with the injection of gases free of or poor in H_2 at a temperature only slightly below that in the reaction space, at one or more points behind the first third of the reaction space, characterized by injecting these gases in such quantities that the H_2 pressure is reduced to one-half or less.

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR THE PRESSURE HYDROGENATION OF COALS, TARS, MINERAL OILS, ETC.

German Patent 722405
Class 12o, Group 1o5
29 December 1931

Issued to
I. G. Farbenindustrie, A. G.
Frankfurt A. M.

Dr. Mathias Pier, Heidelberg,
Dr. Walter Krönig, Ludwigshafen/Rh., and
Dr. Ernst Donath, Mannheim.

DRP 722405

In the production by pressure hydrogenation of particularly low boiling hydrocarbons from coals, tars, mineral oils, their products of distillation and extraction as well as residues, it is already known that catalysts containing halogen or its compounds may be used.

It was found that particularly good results are obtained if halogen compounds containing solid metalloids, together with compounds of the metals of the 5th and 6th groups of the periodic system or oxides, sulfides, or phosphates of other metals, are used as catalysts. These catalysts differ from those known in their increased splitting and hydrogenation effect. The latter is particularly evident with the highest molecular constituents of the feed materials. The process is of importance, for example, in the processing of high boiling feed materials to middle oil with recycling of the constituents above the end boiling point of the middle oil, because, besides splitting, far-reaching hydrogenation takes place when the catalysts mentioned are used, even at high temperatures, so that no H_2-poor products of condensation occur in the constituent continuously recycled to the reaction vessel. The catalysts have this further advantage that the split products of reaction below the boiling range of the feed materials are not saturated with H_2. For example, in the processing of middle oils in the vapor phase H_2-poor gasolines are produced, and in the processing of high boiling feed materials in the liquid phase, H_2-poor middle oils and low boiling hydrocarbons are obtained, while the higher boiling products show an appreciably greater H_2-content than the feed material.

The most important halogen compounds under consideration are those containing carbon and hydrogen, particularly the bromine and chlorine compounds, as, for example, carbon-tetrachloride, chloroform, iodoform, bromoform, the chlorine, bromine or iodine compounds of benzol naphthalene, toluol, xylol, phenol, cresol, anthraquinone and nitrobenzol, as well as methyl-, ethyl-, methylene-, ethylene-chloride, bromide or-iodide, also fluoroform, fluorbenzol and fluor-naphthalene or substances containing these compounds

Halogen compounds of solid metalloids other than carbon, particularly of phosphor, sulfur, selenium, tellurium, arsenic, autimony, silica, titanium, zircon or boron are also very effective catalysts, because they contain a happy combination

DRP 722405

In the production by pressure hydrogenation of particularly low boiling hydrocarbons from coals, tars, mineral oils, their products of distillation and extraction as well as residues, it is already known that catalysts containing halogen or its compounds may be used.

It was found that particularly good results are obtained if halogen compounds containing solid metalloids, together with compounds of the metals of the 5th and 6th groups of the periodic system or oxides, sulfides, or phosphates of other metals, are used as catalysts. These catalysts differ from those known in their increased splitting and hydrogenation effect. The latter is particularly evident with the highest molecular constituents of the feed materials. The process is of importance, for example, in the processing of high boiling feed materials to middle oil with recycling of the constituents above the end boiling point of the middle oil, because, besides splitting, far-reaching hydrogenation takes place when the catalysts mentioned are used, even at high temperatures, so that no H_2-poor products of condensation occur in the constituent continuously recycled to the reaction vessel. The catalysts have this further advantage that the split products of reaction below the boiling range of the feed materials are not saturated with H_2. For example, in the processing of middle oils in the vapor phase H_2-poor gasolines are produced, and in the processing of high boiling feed materials in the liquid phase, H_2-poor middle oils and low boiling hydrocarbons are obtained, while the higher boiling products show an appreciably greater H_2-content than the feed material.

The most important halogen compounds under consideration are those containing carbon and hydrogen, particularly the bromine and chlorine compounds, as, for example, carbon-tetrachloride, chloroform, iodoform, bromoform, the chlorine, bromine or iodine compounds of benzol, naphthalene, toluol, xylol, phenol, cresol, anthraquinone and nitrobenzol, as well as methyl-, ethyl-, methylene-, ethylene-chloride, bromide or iodide, also fluoroform, fluorbenzol and fluor-naphthalene or substances containing these compounds

Halogen compounds of solid metalloids other than carbon, particularly of phosphor, sulfur, selenium, tellurium, arsenic, antimony, silica, titanium, zircon or boron are also very effective catalysts, because they contain a happy combination of two inherently catalytic constituents. The following such compounds enter into consideration: phosphor-trichloride, -tribromide,-pentabromide,-sulfochloride,-subiodide,-triiodide, -sulfur-monochloride, sulfur-tetrachloride, selenium-monochloride, -tetrachloride,-monobromide,-tetrabromide,-iodide, tetraiodide, tellurium-monochloride,-tetrachloride,-monobromide,-tetrabromide, -subiodide,-tetraiodide, arsenic-trichloride,-tribromide, -triiodide, antimony-trichloride,-pentachloride,-tribromide, -triiodide, boron-trichloride, as well as metal or ammonium-tellurium-bromide,-iodide or -chloride, or the corresponding antimony compounds, or silica-tetrachloride,-fluoride, or hydrofluorocilicic acid.

According to this invention, the halogen compounds are used together with compounds of metals of the fifth and sixth groups of the periodic system or oxides, sulfides or phosphates of other metals, as, for example, the oxides, sulfides, nitrides, phosphates and halogenides of vanadium, molybdenum, tungsten-chromium and uranium, and the oxides, sulfides or phosphates of copper silver, magnesium, zink, tin, cadmium, silica, aluminum, titanium, manganese, nickel, rhenium, cobalt or iron.

Feed substances under consideration are brown coal, bituminous coal, peat, oil shale, tars, mineral oils or their fractions, or split or pressure hydrogenation products. These catalysts are also very well suited for processing asphalts and resins, as well as for refining or improving hydrocarbon oils, such as gasolines, benzol, middle oils or lubricating oils, and dehydrogenation of hydrocarbons.

The reaction, in the liquid as well as the vapor phase, proceeds under the usual conditions of pressure and temperature, e.g. at temperatures from 250 to 600°C and pressures from 20 to 1000 atm.

The catalyst is added either before entry into the preheat zone or during the preheating or the reaction. The constituents of the catalyst mixture may be added to the substances to be treated at various points. The use of carriers, such as active coal, pumice, adtive silicic-acid or pottery fragments is also of advantage. It may also be advantageous to arrange the non-halogen constituent of the catalyst, if solid, by itself in a fixed position in the reaction vessel and to pass the feed substances with volatile halogen compounds over them. Liquid halogen compounds may simply be mixed with the substances to be treated. For example, coal may be drenched with the liquid halogen compound, which guarantees an excellent distribution in the hydrogenation substance.

The quantity of catalyst to be added varies within the limits of 0.01 to 10%, preferably 0.01 to 3%.

It has also been advantageous to add about 0.5 to 5% hydrogen-halide, for example, hydrogen-bromide or - chloride to the hydrogenation gas, which should be used in a flowing condition in order to obtain maximum yields. In the presence of metallic sulfides it may also be of advantage to add a little H_2S to the hydrogenation gas.

The catalysts mentioned are particularly effective in the vapor phase, in which the feed substance is primarily middle oil. A further advantage of the catalysts may be seen in that the feed substances mixed with them form no polymerization products, as is often the case with the use of free halogen, such as iodine. When the described catalysts are used, a high grade anti-knock gasoline and a middle oil exceptionally rich in hydrogen are obtained, which later can be used as illuminating or diesel oil or may be recycled to the reaction vessel for complete conversion to gasoline.

It is, to be sure, already known that metalloid, such as carbon, phosphorus, arsenic, tellurium or halogens, in free or combined form, may be used as catalysts in the pressure hydrogenation of coals, tars and mineral oils at high temperatures. By comparison, according to this invention, certain halogen compounds, namely those with solid metalloids, are used together with certain other compounds. The particular advantages of these catalysts may be seen in the following examples. Compared to the known use of metallic halogenides, they have the advantage of lower polymerizing effect, particularly in the processing of asphaltic substances.

Example 1.

Central German brown coal is finely pulverized and drenched with a solution of ammonium-molybdate, so that the coal contains 0.02% molybdic acid. The pulverized coal is then pasted with an oil boiling above 300°C and obtained from the same coal by pressure hydrogenation in the proportion of 1:1 and, together with hydrogen at a pressure of 250 atm, conducted through a gas-fired preheater, in which the substances taking part in the reaction are heated to 455°C. Chlorobenzene is injected into the reaction converter in such a quantity that the coal paste in the converter contains 0.1% chlorine. Ninety-five percent of the carbon input is converted into valuable hydrocarbons. The asphalt content in the residue is reduced to about one half by the catalytic action of the chlorobenzene.

Chlorinated paraffin may also be used instead of the above name chlorobenzene.

Example 2.

The middle oil fraction from Volkenroda petroleum is obtained by distillation. This is heated together with H_2 in a gas-fired preheater to 480°C at a pressure of 200 atm. Before entry into the reaction converter 1% ethylene-chloride, based on the middle oil, is added. This mixture is then passed over the molybdenum-bromide catalyst arranged in a fixed position in the reaction vessel. In a single pass of this mixture thru the reaction converter, a product is obtained consisting of 50% gasoline with heptane and 50% of a middle oil with a higher H_2-content than the feed oil, and which can be used for illuminating or diesel oil.

In place of ethylene-chloride, ethylene-bromide, bromoform or methylene-bromide may also be used.

Example 3.

Bituminous coal is finely ground and mixed with 1% finely distributed iron-sulfide. This mixture of catalyst and powdered coal is then mixed with a heavy oil originating from the same coal in the proportion 1:1 and, together with H_2 at a pressure of 250 atm, heated to 460°C in a gas-fired coil preheater. The reaction feed then passes into an enlarged high pressure vessel, where 0.1% arsenic-trichloride, based on the coal paste, is added at the inlet. The carbon in the coal is hereby converted 94% into valuable hydrocarbons with an anti-knock value corresponding to a mixture of 76% iso-octane and 24% normal octane. The asphalt content of the residue is reduced about 40%, compared to working without arsenic-trichloride.

Example 4.

Brown coal is finely pulverized and drenched with a watery solution of ammonium-molybdate, so that the coal contains 0.02% molybdic acid. The coal is then mixed with a heavy oil originating from the same coal in the proportion of 1:1 and heated, together with H_2 at a pressure of 250 atm, in a preheater to 455°C. The substances participating in the reaction are then conveyed to a hydrogenation vessel after adding 0.5% sulfur-monochloride, based on the coal paste.

The carbon in the coal is converted 97% into valuable hydrocarbons, mostly in liquid form. The asphalt content of the residue is about 40% less than when the reaction is conducted without sulfur-monochloride.

Example 5.

Bituminous coal is finely pulverized and drenched with a solution of tin oxalate, so that the coal contains 0.06% tin oxide. The coal powder is then pasted with a heavy oil originating from the same coal in the proportion of 1:1 and heated, together with H_2 at a pressure of 250 atm, in a preheater to 460°C. In the reaction converter connected to the preheater, 0.3% selenium-tetrabromide is added to the coal paste. Ninety-six percent of the carbon in the coal is hereby converted into mainly liquid hydrocarbons. The asphalt content is reduced 35% compared to operating without selenium-tetrabromide.

Example 6.

Hannover crude oil boiling above 325°C is mixed with 2% aluminum oxide and together with H_2 at a pressure of 250 atm, heated to 470°C, and then conveyed into a reaction converter. Before entry of the reaction feed into the preheater, 1.5% ethylene-bromide is added to the crude oil. The product leaving the converter consists of 10% high boiling residue and 90% of a distillate of which 50% boils to 325°C. If the reaction is conducted without the addition of ethylene-bromide, only 85% of the feed can be processed per unit of space and time in order to obtain the same results.

Example 7.

A Thüringer crude oil boiling above 325°C is mixed with 1% iodo-benzene, heated to 460°C together with H_2 at a pressure of 250 atm, and conducted thru a high pressure vessel. The liquid product of reaction consists of 8% high boiling residue and 92% of a distillate, 45% of which boils up to 325°C. In order to obtain the same yield without iodo-benzene, the thruput per unit of space and time could be only 75%.

Example 8.

High volatile Ruhr coal is finely ground and drenched with a solution of tin oxalate, so that the coal contains 0.05% tin oxide. The coal is then pasted with a heavy oil obtained from the same coal by pressure hydrogenation in the proportion of 1:1 and heated in a gas-fired preheater to 445°C, together with H_2 at a pressure of 250 atm. Immediately before the preheater 0.85% carbon-tetrachloride, based on the coal, is added to the coal paste. The reaction constituents are then conveyed to an enlarged reaction vessel, where they reach a temperature of 460°C. The coal conversion equals 96%. The oil obtained contains 95% gasoline and middle oil, and the heavy oil contains 8% asphalt. If the reaction is conducted without carbon-tetrachloride, under otherwise equal conditions, the conversion is only 91% and the heavy oil contains 12% asphalt.

Example 9.

If the vapors of a middle oil obtained from German petroleum by pressure hydrogenation are passed over tungsten-hexachloride together with H_2 at a pressure of 200 atm and a temperature of 430°C and 1% ethylene-chloride is added to the feed before entry into the reaction converter, a product is obtained cntaining 52% constituents boiling to 185%. If tungsten-hexachloride alone is used, a product containing 40% boiling to 185°C is obtained, and if ethylene-chloride alone is used, a product containing only 15% constituents boiling to 185°C is obtained.

Patent Claims.

1. Process for the pressure hydrogenation of coals, tars and mineral oils, their products of distillation, splitting and extraction, as well as residues, in the presence of catalysts containing halogen, characterized by using halogen compounds containing solid metalloids, together with compounds of metals of the fifth and sixth groups of the periodic system, or oxides, sulfides or phosphates of other metals, as catalysts.

2. Process according to Claim 1, characterized by using halogen compounds containing solid metalloids, which contain carbon and hydrogen.

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T-283
Ernst Donath

Alternative Flow Sheets
Improved Coal Hydrogenation Plant

(Described in the paper, "Thermal Efficiency of Coal Hydrogenation - Present and Future".)

The improved coal hydrogenation plant consists of 700 atm. liquid phase and directly attached 700 atm. vapor phase units. For the liquid phase, "single-stage" conditions are used, the main product being middle oil and gasoline. For the vapor phase, a splitting catalyst working at high temperature (about 500° C. = 930° F.) is used.

Improvements in yields and converter space requirements seem attainable when the liquid phase is operated under such conditions that the new-formed oil consists of about 25% gasoline, 25% middle oil and 50% heavy oil. The presence of heavy oil necessitates the use of a vapor phase catalyst with less splitting and more hydrogenating activity working at about 450° C. To convert the product from this catalyst into gasoline, either a separate splitting hydrogenation step or a catalytic cracking step is provided. In the latter case, the cracked recycle oil is rehydrogenated together with the coal oil.

In the proposed flow diagram, one part of the gases and vapors of the liquid phase hot catchpot is directly (without pressure release) conducted into the gas phase. The other part is cooled and after removal of liquid phase gasoline and naphtha, which also goes into the vapor phase, is used as pasting oil.

The proposed alternative offers the possibility to produce high cetane diesel fuel and to recover phenols without an essential change in the flow of the products.

The following Table I contains the essential data estimated for the three different flow diagrams. Further details are listed in Appendices 1 - 4, and for the catalytic cracking in Appendix 5.

TABLE I

Details in Appendix Liquid Phase Vapor Phase	(2) Middle oil Splitting Cat.	(3) Heavy Oil Prehydrog.cat. Splitting cat.	(4)&(5) Heavy Oil Prehydrog. cat. Cat.Cracking
Wt. % gasoline/maf coal	550	62.1	56.7 1/
Gasoline O.N.M.M.	77	72 5/	75
Gasoline O.N.R.M.	87	73	83
M^3 H_2/te coal 2/	1380	1425	1360
M^3 H_2/te gasoline	2500	2300	2400
for 250 tonnes/h = 50,000 bbls./day gasoline			
maf coal f.hydrog.tonne/h	455	405	440
Hydrogen m^3/h	625,000	575,000	600,000
Converter volume m^3,L/Vph.	830/550	500/230 + 230 3/	550/475
Number of converters,L/Vph.	42/28	25/12 + 12 3/	28/24
Number of stalls	10	9 = 6 + 3 3/	8
Converters in ea. LØ Stall	4	4	3.5
Converters in ea. VØ Stall	3	2 + 4 3/	3
Paste pumps tonne/h	1050	935	1020
V.Ph. pumps tonne/h	365	390	485
Total injection tonne/h	1415	1325	1505
Recycle Gas $10^6 m^3$/h L/VPh.	161/-	145/0.52	1.5 3/-
Distillation tonne/h	615	600	555 4/
Catalytic cracking, total thruput tonne/h/bbl./day	-	-	435

1/ Including polymer-gasoline. This yield can be increased by about 2.5% using alkylation instead of polymerization.

2/ 0°C., 760 mm Hg., based on H absorbed + 15% loss.

3/ Splitting phase.

4/ Besides 390 t/h to be distilled in catalytic cracking.

5/ Octane number may be bettered by use of improved catalysts, which have been used in small scale work.

APPENDIX 1

Basic Flow Sheet Data

L.Ph. main product:	M.O. (Appendix 2)	M.O.+ H.O. (1:1) (Appendix 3)
Liquid Phase		
Coal conversion	96%	96%
% C as gas/C in oil & gas	22.5	19.0
Maf coal thruput kg/l.hr.	0.55	0.8
Pasting oil % M.O.	5	50
% Solids in H.O.L.D.	44	44
% H.O. loss/maf coal	4	4
Composition of new-formed oil %-200°C.= 392° F.	21	25% (Net H 13.8)
200-325°C.= 617° F.	79	25% (Net H 10)
325°C.= 617° F.	0	50% (Net H 9.5)

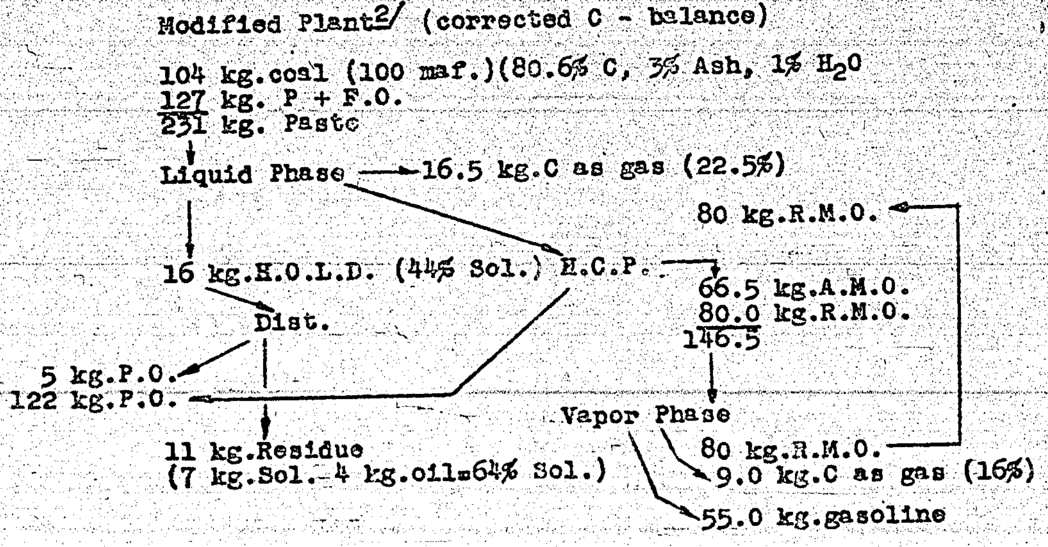
Vapor Phase Catalyst	Silicate support	Sulphides on Alumina	Silicate Support **
Gasoline kg/l.hr.	0.45	0.24	0.75
Thruput kg/l.hr.	1.5	1.2*	1.5
M^3 gas/kg feed	2.5	1.5*	1.5
% C as gas/gasoline + gas	16	16.5	10
% C as gas/total thruput	15.5	3.5	15.8

* - Including eventually recycle oil from catalytic cracking.

** - For presaturated oils.

APPENDIX 2

(Product 100% M.O. + Gasoline)



	Liters converter vol. per 100 kg.maf.coal	 100 kg.gasoline
Coal thruput 0.55 =	182	330
Gasoline space time yield 0.45	122	222
Total	304	552

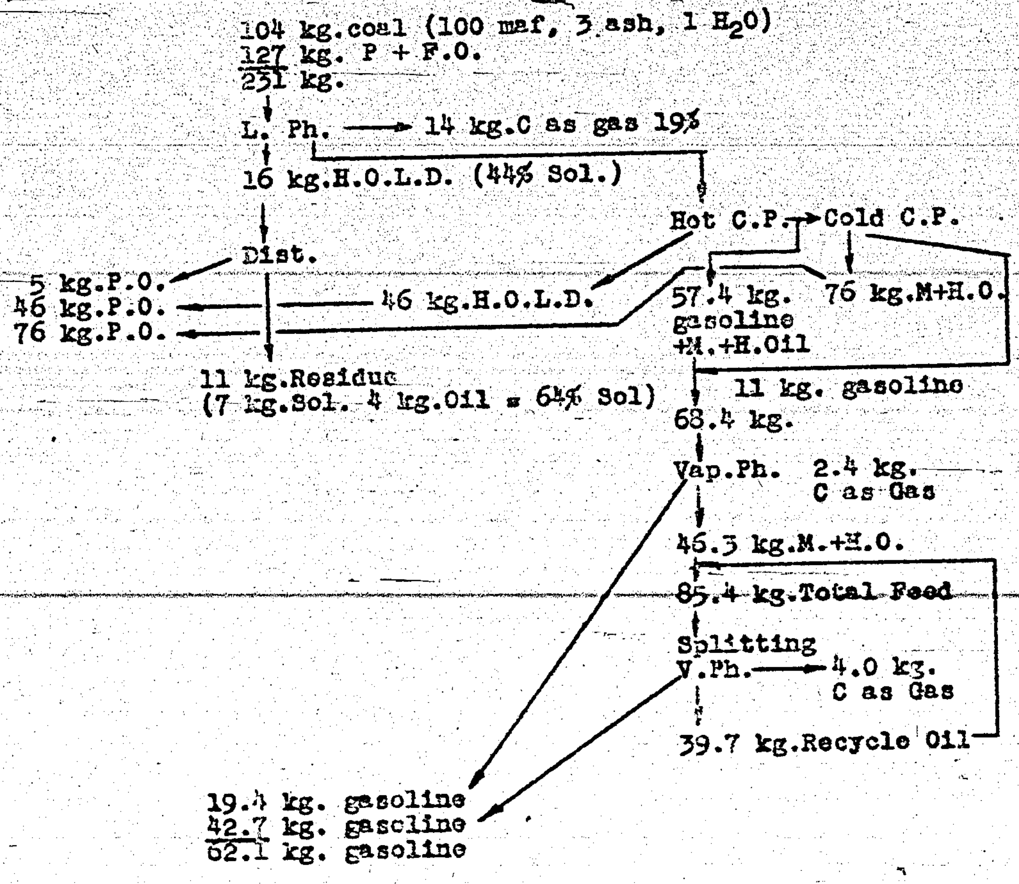
Hydrogen consumption 1/ per	tonne coal	tonne gasoline
kg. absorbed	107	194
kg. loss (15%)	16	29
Total m^3	1380	2500

1/ Grams net H/100 grams C: Coal 4.3, coal residue 4.3, Gasoline 15.0, Gas 25.2, H.O.Loss 9.0.

2/ Process described in paper.

APPENDIX 3

Modified Plant L.Ph.Product 50% M.O. + Gasoline
50% H.O. + 2-Step Vap. Phase



APPENDIX 3 (Continued)

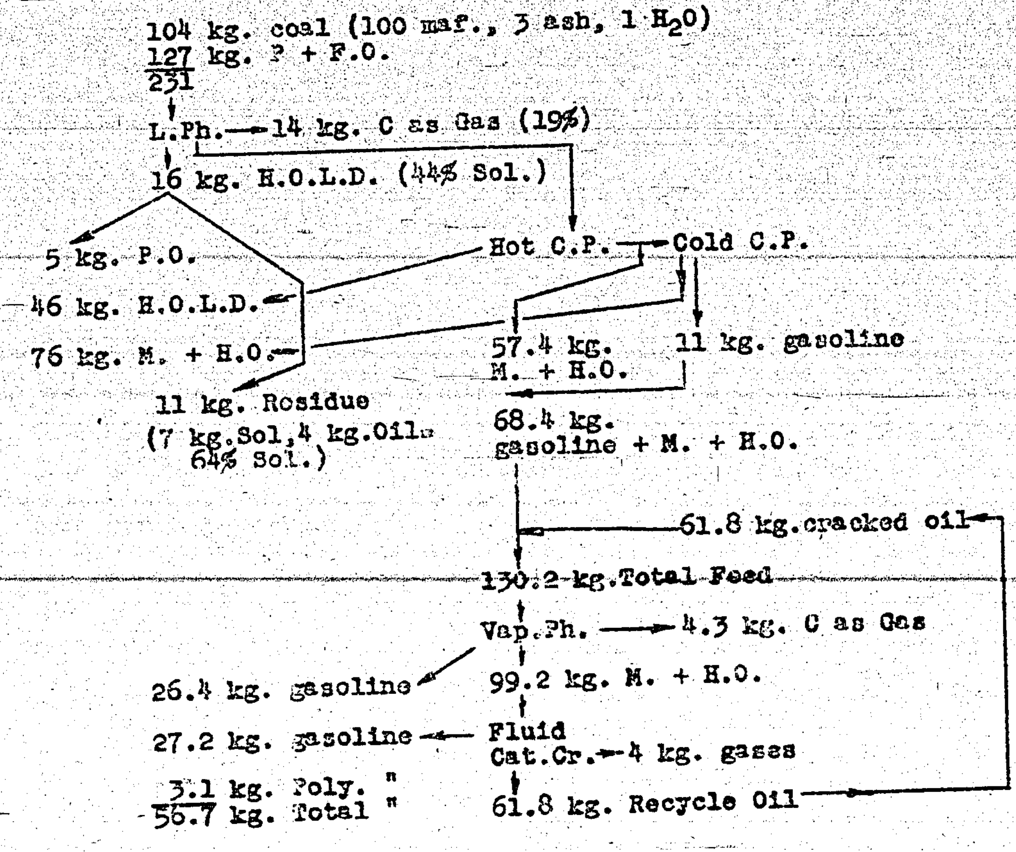
		Liters converter vol. per	
		100 kg.maf.coal	100 kg.gasoline
Coal thruput	0.8	125	201
Vap. Phase thruput	1.2	57	92
Splitting V.Ph. thruput	1.5	57	92
	Total -	239	385

Hydrogen consumption[1/] per	tonne coal	tonne gasoline
kg. absorbed	110	177
kg. loss (15%)	17	27
Total m^3	1425	2300

[1/] Grams net H/100 grams C: V.Ph. gasoline 16.1, Splitting V.Phase gasoline 17.5, Splitting V.Ph. gas 21.2.

APPENDIX 4

Modified Plant Liquid Phase Product 50% M.O. + Gasoline
50% H.O.
Vapor Phase and Cat. Cracking



APPENDIX 4 (Continued)

		Liters converter vol. per	
		100 kg.maf.coal	100 kg.gasoline
Coal thruput	0.8	125	220
Vap. Phase thruput	1.2	108	190
Total		233	410

Hydrogen consumption[1] per	tonne coal	tonne gasoline
kg. absorbed	106	186
kg. loss (15%)	16	28
Total m^3	1360	2400

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[1] Grams net H/100 grams C: Hydro-gasoline 16.1, Vap.Ph. M. + H.O. 15.2, cracked recycle oil 14.4.

APPENDIX 5

Fluid Cat. Cracking Prehydrogenated Coal, M + H Oil, based on Kellogg data for petroleum oils and extrapolated to lower conversion per pass, using figures with recycle.

	Data for Petroleum Oil			Estimated for Hydrogenated Oil	
Feed Sp.Gr.	0.880			0.870	
50% Point	(325°)			275°	
% H_2	13.2			13.1	
		Extrapolated			
Yields Wt. %:					
Coke	4.5	3.0	2.0	3.1	2.1
Dry Gas	7.0	3.6	2.8	3.7	2.9
C_4	7.4	5.0	3.5	5.1	3.6
Gasoline (C_4 free)	30.3	25.9	21.2	25.9	21.2
Cycle Oil	50.8	62.5	70.5	62.2	70.2
Gasoline 10#	32.2	27.5	22.5	27.5	22.5
Residual C_4	5.5	3.4	2.2	3.5	2.3
Poly-gasoline from C_4	4.4	3.0	2.1	3.1	2.2
Total gasoline	36.6	30.5	24.6	30.6	24.7
% Loss/10# gasol. + Loss	34.5	26.5	23.5	27.5	24.5
Loss/total " "	25.5	18.5	16.5	19.0	17.0
Gasoline Sp.Gr.	0.751	0.75	0.75	0.75	0.75
%-100°	54	52	51	50	50
O.N.M/R	82/96	81/95	81/85	81/95	81/95
Cycle Oil Sp.Gr.	0.898	0.883	0.882		
50% P °C.	280°	(285)	(290)	(240)	(250)

C & H Balance Cat.Cracked - Arabian Gas Oil

Feed 100 86.8% C 13.2% H

	(a)			(b)			(c)		
Grammes	Prod.	C	H	Prod.	C	H	Prod.	C	H
Coke	4.5 1/	4.28	0.22	3.0	2.85	0.15	2.0	1.90	0.10
Dry Gas	7.0 2/	5.66	1.34	3.6	2.90	0.70	2.8	2.26	0.54
C_4	7.4 3/	6.27	1.13	5.0	4.22	0.78	3.5	2.96	0.54
Gasoline	30.3 4/	26.20	4.10	25.9	22.40	3.50	21.2	18.34	2.86
Cycle Oil	50.8 5/	44.52	6.28	62.5 5/	54.53	7.97	70.5 5/	61.45	9.05
	100.0	86.93	13.07	100.0	86.90	13.10	100.0	86.91	13.09

C & H Balance Cat.Cracked Hydrogenated Oil

	Prod.	C	H	Prod.	C	H
Feed	100.0	86.9	13.1	100.0	86.9	13.1
Coke	3.1 1/	2.95	0.15	2.1	2.00	0.10
Dry Gas	3.7 2/	2.98	0.72	2.9	2.34	0.56
C_4	5.1 3/	4.30	0.80	3.6	3.04	0.56
Gasoline	25.9 4/	22.40	3.50	21.2	18.34	2.86
Cycle Oil	62.2 6/	54.35	7.85	70.2 6/	61.30	8.90
	100.0	86.98	13.02	100.0	87.02	12.98

1/ 95% C, 5% H

			C	H		C	H
2/ 33	CH_4		75.0%	25.0%	=	24.8	8.2
33	C_2	50% Olef.	82.8	17.2		27.3	5.7
34	C_3	70% Olef.	84.5	15.5		28.7	5.3
100						80.8	19.2

3/ 60% Olefins = 84.5% C, 15.5% H

4/ 86.5% C, 13.5% H

5/ (a): 87.7% C, 12.3% H (b): 87.3% C, 12.7% H (c): 87.2% C, 12.8% H

6/ (b): 87.4% C, 12.6% H (c): 87.3% C, 12.7% H

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The Temperature Distribution in the Louisiana Vapor Phase Stall

By: Dr. E. E. Donath

For the calculation of the temperatures in the individual catalyst beds, the following flow sheet data were used:

Thruput:	2691#/hr fresh feed 4500#/hr recycle feed 7191#/hr total feed = 3.27 tonne/hr.	
Recycle Gas:	5238#/hr = 343,500 c.f./hr	= 9700 m^3/hr
Hydrogen Absorbed:	147.8#/hr	= 67 kg/hr
BTU/# absorbed Hydrogen:	11,650	= 6.5 cal/g H
Specific Heat:	1.2 BTU/# gas, °F.	= 0.3 kcal/m^3, °C.
	0.7 BTU/# Total Feed, °F.	= 0.7 kcal/kg, °C.

Length of catalyst beds:

Bed No.	1	2	3	4	5	6
Length	4'3"	4'5"	4'8"	4'11"	5'2"	5'7"
% of catalyst	14.7	15.3	16	17	17.8	19.2

This gives the following specific data:

3.0 m^3 injection gas/kg. total feed
133 kcal heat of reaction/kg total feed

The heat content of 1 kg. total feed and 3 m^3 injection gas being 1.6 kcal/°C., the total temperature increase of the reactants, due to the heat of the reaction would be $\frac{133}{1.6}$ = 83°C.

For a temperature reduction of 1°C. of the reactants 0.0116 m^3 cooling gas are necessary.

In order to compute the temperature increase in each bed, the curve in Figure 1, for the distribution of the heat of the reaction, in the catalyst, was used. This curve was derived from 300 atm. operation in vapor phase, no actual data for the 700 atm. vapor phase being available. The temperature of 490° C. was chosen to some extent arbitrarily as the normal reaction temperature, and with the heat of the reaction from

Figure 1, the temperature rise, the lowest and highest temperatures, and the cooling gas requirements in Table 1(a) were calculated. As this distribution of the reaction and the bed outlet temperatures are unsatisfactory, the temperature increases in each bed were changed in order to get a slight increase in the outlet temperatures of the successive beds, as shown in Table 1(b). The temperature increase in each bed in Table 1(a), divided by that in Table 1(b), gives the relative reaction velocity. For the calculation of the average bed temperatures from the relative reaction velocities Figure 4 was used. Figure 4 was based on a doubling of the reaction velocity for each 10° C. temperature increase, and not on the unknown actual temperature coefficient. Consequently, the average bed temperatures from Table 1(b) have rather a relative value and show the trend of bed temperatures using changed reaction rates in the individual beds.

During the operation of a vapor phase unit, the activity of the catalyst in the first bed is likely to be impaired. Therefore, the figures in Table 2 are calculated assuming that the catalyst in this bed has only 50% of the activity in comparison to Table 1.

Furthermore, Table 3 contains data based on the heat distribution curve from Figure 2, where the amount of reaction in the first two beds is arbitrarily reduced by 20% in comparison to Figure 1. Table 4 contains figures based on Figure 3 where the heat of reaction in the first bed is assumed to be 25%, and in the second bed 10% higher than in the corresponding beds Figure 1.

In the following Tables A - D, the data for the best temperature distribution from Table 1 to 4 are summarized. These tables contain also the estimated increase of the outlet temperature, if the inlet temperature of an individual bed rises 4° C. These data are a measure of the relative temperature stability of each bed. They are obtained from Figure 5, this being derived from Figure 4, assuming constant activity over one bed. The outlet temperature of the bed will be obtained from Figure 5 by determining the abscissa length corresponding to the temperature increase in the bed and applying the same abscissa length to the increased inlet temperature. As the temperature coefficient from Figure 4 was used for Figure 5, the obtained temperature rise can only be used for comparison.

Table A shows that a moderate stability of beds 1 - 3 is obtainable with highest temperatures of 500° in beds 4 - 6. An increase of 4° C. at the inlet of bed 1, e.g., would increase the outlet temperature by an estimated 19° C. This would necessitate an increase of the cooling gas quantity before bed 2 of 0.22 m^3/kg. total feed, corresponding to 700 m^3/hr., or 25,000 $ft.^3$/hr.

540

Bed No.	Inlet Bed Temperature ° C.	Outlet Bed Temperature ° C.	Temp. rise ° C.	Cu.meters cooling gas/kg. total feed	Outlet temperature rise ° C. when inlet temp. rises 4° C.
(A) Heat distribution as for 300 atm.vap.ph.(See Table 1(b).					
1	477	494	17	-	19
2	479	496	17	0.17	19
3	481	498	17	0.17	19
4	487	500	13	0.13	13
5	488.5	500	11.5	0.13	11
6	492.5	500	7.5	0.09	7
Total			83.0	0.69	
(B) Bed 1 has 50% of the activity in comparison to (A) (See Table 2(b).					
1	486.5	500	13.5	-	13
2	479	497	18.0	0.24	21
3	482	500	18.0	0.17	21
4	487	501	14	0.14	14
5	489	501	12	0.14	12
6	492.5	500	7.5	0.09	7
Total			83.0	0.78	
(C) Flatter curve (See Table 3(b) and Figure 2).					
1	481	496.5	15.5	-	16
2	481.5	497.0	15.5	0.17	16
3	482.5	497.0	14.5	0.17	15
4	484.0	497.0	13.0	0.15	13
5	485.0	497.0	12.2	0.14	12
6	486.0	498.5	12.3	0.13	12
Total			83.0	0.76	
(D) Steeper curve (See Table 4(b) and Figure 3).					
1	474.5	492.5	18	-	21
2	478.0	496.0	18	0.17	21
3	484.0	510.5	16.5	0.14	19
4	489.0	501.0	12	0.13	12
5	493.0	503.5	10.5	0.09	10
6	495.0	503.0	8.0	0.10	7
Total			83.0	0.63	

A somewhat greater stability of beds 1 - 3 could be obtained by an increase in the temperatures of beds 4 - 6. Table (B)(where catalyst in bed 1 has 50% of the activity) shows that the stability of beds 2 and 3 at the same thruput is smaller, and that higher temperatures are required.

The flatter curve used for Table (C) gives more stable beds and lower bed outlet temperatures than those in the previous table.

The steeper curve from Table (D) gives moderately stable beds 1 and 2 with outlet temperatures of over 500° C. in beds 3 - 6.

By a reduction of the size of the beds 1 and 2, an improvement of the temperature control in case (D) could be obtained. However, this would mean poorer temperature control in cases (B) and (C) and probably no improvement in case (A).

The above given data indicates that the operation of the Louisiana vapor phase stall with six catalyst beds will require careful control of temperature, thruput, and gas, especially cooling gas quantities. In order to improve the temperature stability of the first catalyst beds, an increase of the gas and recycle feed rate should be possible.

The available data for the distribution of the heat of reaction are not very exact. They do not seem to indicate that a change in the design bed size would give an overall improvement of temperature performance.

In the appendix, some data for a seven-bed convertor are compared with corresponding data in German plants. As the data for the heat of the reaction, etc., used in this comparison, deviate to some extent from those for the Louisiana flow sheet, they are also not directly comparable with the data used above.

TABLE I.

Performance of the individual beds (curve from Figure 1).

Bed No.	Relative reaction velocity	Corresponding average temp. °C.	% of total reaction heat	Corresponding temperature increase ° C.	Lowest °C. temperature in each bed	Highest °C. temperature in each bed	Cu.meters cooling gas per kg. total feed
(a) Equal average temperatures.							
1	1.0	490	26.8	22.2	479	501	-
2	1.0	490	24.4	20.2	480	500	0.24
3	1.0	490	20.3	16.9	482	499	0.21
4	1.0	490	12.5	10.4	485	495	0.16
5	1.0	490	10.5	8.7	486	495	0.10
6	1.0	490	5.5	4.6	488	493	0.08
			100.0	83.0			0.79
(b) Rising average bed temperatures.							
1	0.77	486	20.4	17.0	477	494	-
2	0.84	487.5	20.4	17.0	479	496	0.17
3	1.01	490.0	20.4	17.0	482	499	0.17
4	1.25	493.0	15.7	13.0	487	500	0.13
5	1.32	494	13.9	11.5	488.5	500	0.13
6	1.63	497	9.2	7.5	492.5	500	0.09
			100.0	83.0			0.69

TABLE II

Performance of the individual beds, assuming that the catalyst in bed 1 has only 50% of its original activity (curve Figure 1), or need 10° C. higher temperature.

Bed No.	Relative reaction velocity	Corresponding average temp. °C.	% of total reaction heat	Corresponding temperature increase °C.	Lowest °C. temperature in each bed	Highest °C. temperature in each bed	Cu.meters cooling gas per kg.total feed
		(a) Distribution of reaction as in Table 1(a)					
1	1.0	500	26.8	22.2	489	511	-
2	1.0	490	24.4	20.2	480	500	0.36
3	1.0	490	20.3	16.9	482	499	0.21
4	1.0	490	12.5	10.4	485	495	0.16
5	1.0	490	10.5	8.7	486	495	0.10
6	1.0	490	5.5	4.6	488	493	0.08
			100.0	83.0			0.91
		(b) Nearly constant bed outlet temperatures in beds 2 - 5.					
1	0.61	493	16.2	13.5	486.5	500	-
2	0.89	488	21.7	18.0	479	497	0.24
3	1.06	491	21.7	18.0	482	500	0.17
4	1.35	494	16.9	14.0	487	501	0.14
5	1.38	494.5	14.4	12.0	489	501	0.14
6	1.63	497	9.1	7.5	492.5	500	0.09
			100.0	83.0			0.78

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TABLE III

Performance of the individual beds (flat curve from Figure 2).

Bed No.	Relative reaction velocity	Corresponding average temp. °C.	% of total reaction heat	Corresponding temperature increase °C.	Lowest temperature °C. in each bed	Highest temperature °C. in each bed	Cu.Meters cooling gas per kg.total feed
(a) Equal average temperatures.							
1	1.0	490	20	16.6	482	498.5	-
2	1.0	490	20	16.6	482	498.5	0.19
3	1.0	490	18	14.9	483	498	0.18
4	1.0	490	15	12.5	484	496.5	0.16
5	1.0	490	14	11.6	484.5	496	0.14
6	1.0	490	13	10.8	485	496	0.12
			100.0	83.0			0.79
(b) Slightly rising average and outlet temperatures.							
1	0.93	489	18.7	15.5	481	496.5	-
2	0.93	489	18.7	15.5	481.5	497.0	0.17
3	0.97	489.5	17.4	14.5	482.5	497.0	0.17
4	1.04	490.5	15.7	13.0	484.0	497.0	0.15
5	1.05	491	14.7	12.2	485	497	0.14
6	1.14	492	14.8	12.3	486	498.5	0.13
			100.0	83.0			0.76

TABLE IV

Performance of the individual beds (steep curve from Figure 3).

Bed No.	Relative reaction velocity	Corresponding average temp. °C.	% of total reaction heat	Corresponding temperature increase °C.	Lowest temperature °C. in each bed	Highest temperature °C. in each bed	Cu.meters cooling gas per kg.total feed
		(a) Equal average temperatures.					
1	1.0	490	34	28.2	476	504	-
2	1.0	490	27	22.4	479	501	0.29
3	1.0	490	17	14.1	483	497	0.21
4	1.0	490	10	8.3	486	494	0.13
5	1.0	490	7	5.8	487	493	0.08
6	1.0	490	5	4.2	488	492	0.06
			100.0	83.0			0.77
		(b) Rising outlet temperatures.					
1	0.64	483.5	21.7	18	474.0	492.0	-
2	0.81	487	21.7	18	478.0	496.0	0.17
3	1.17	492	19.9	16.5	484.0	500.5	0.14
4	1.44	495	14.4	12	489.0	501.0	0.13
5	1.81	498.5	12.6	10.5	493.0	503.5	0.09
6	1.9	499	9.7	8.0	495.0	503.0	0.10
			100.0	83.0			0.63

DISTRIBUTION OF THE HEAT OF REACTION IN THE CATALYST CURVE FROM 300 ATM. VAPOR PHASE OPERATION

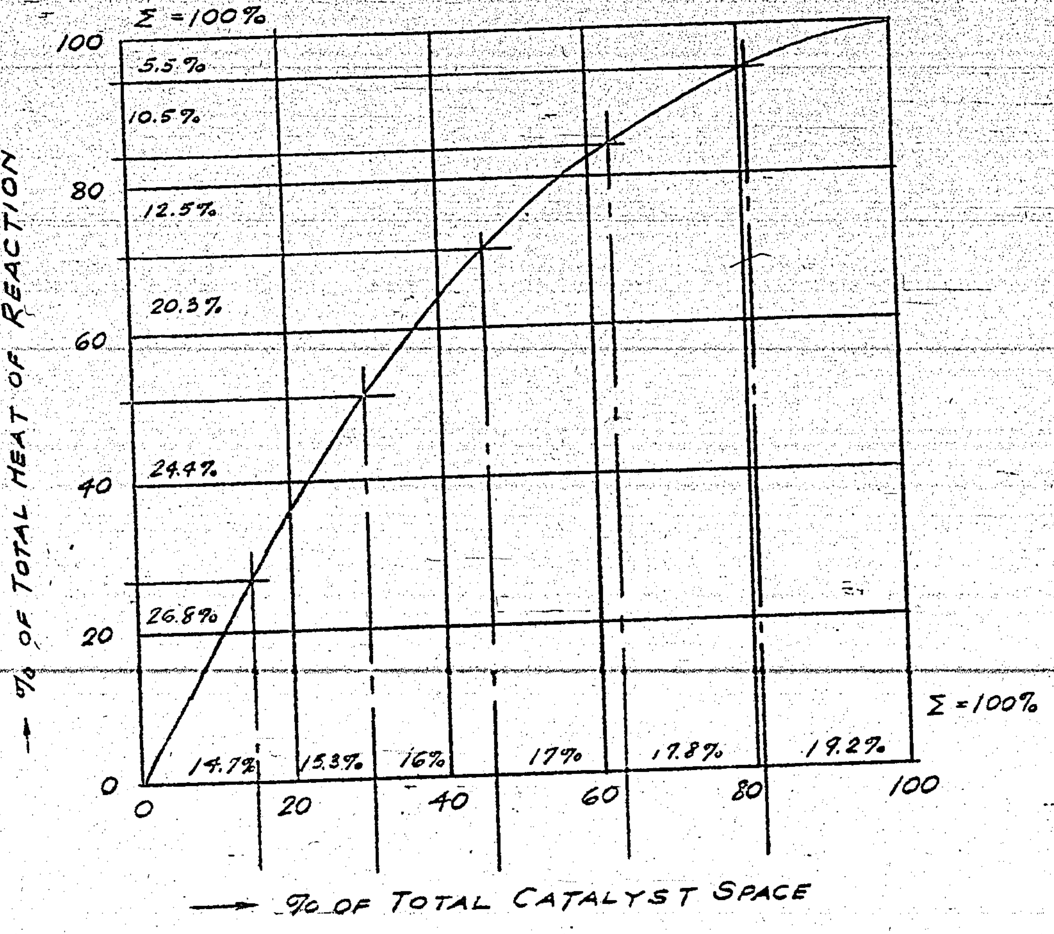


FIG. 1

DISTRIBUTION OF THE HEAT OF REACTION IN THE CATALYST

HEAT OF REACTION IN THE FIRST TWO BEDS ARBITRARILY REDUCED BY 20% IN COMPARISON TO FIGURE 1

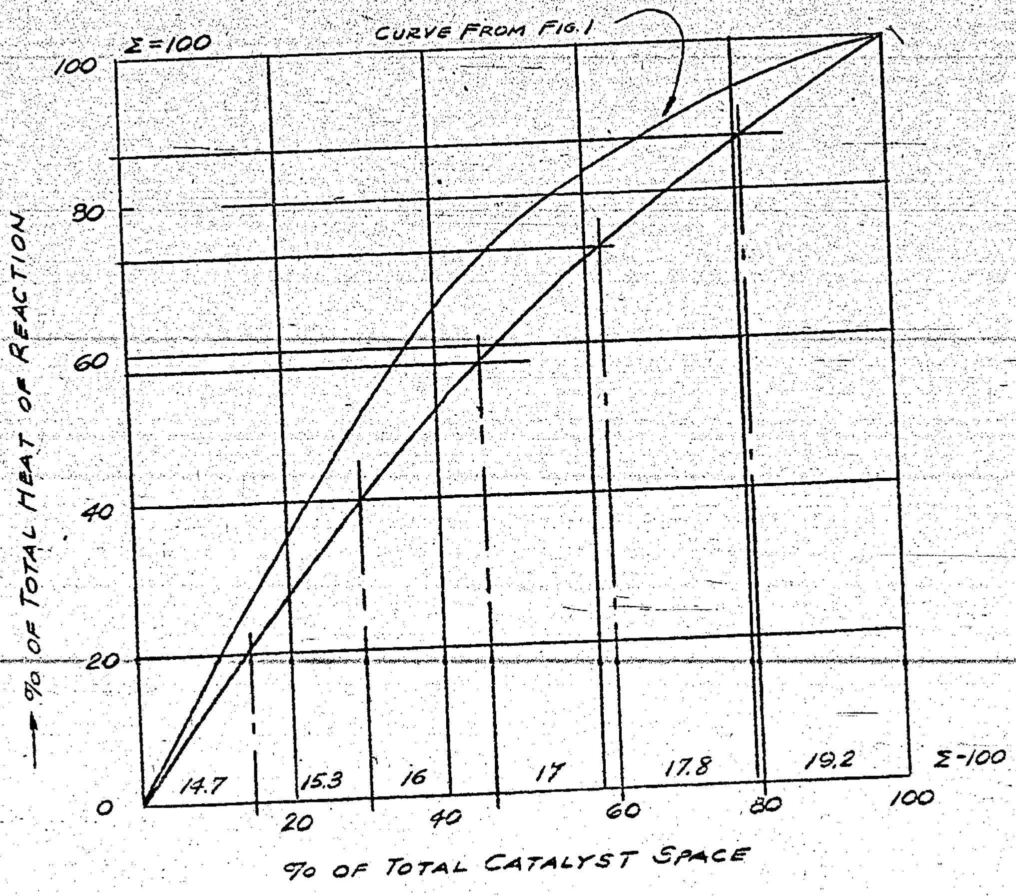


FIG. 2

DISTRIBUTION OF THE HEAT OF REACTION IN THE CATALYST

HEAT OF REACTION ARBITRARILY INCREASED BY 25% IN THE FIRST AND 10% IN THE SECOND BED IN COMPARISION TO FIG. 1

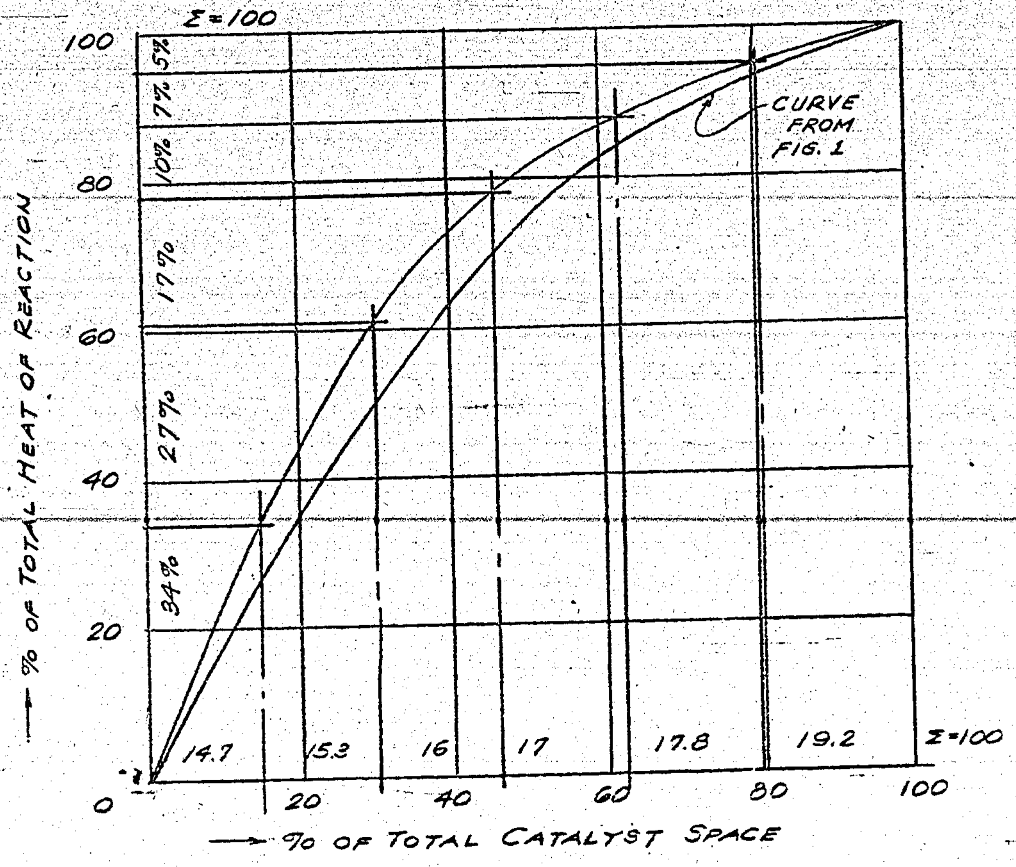


FIG. 3

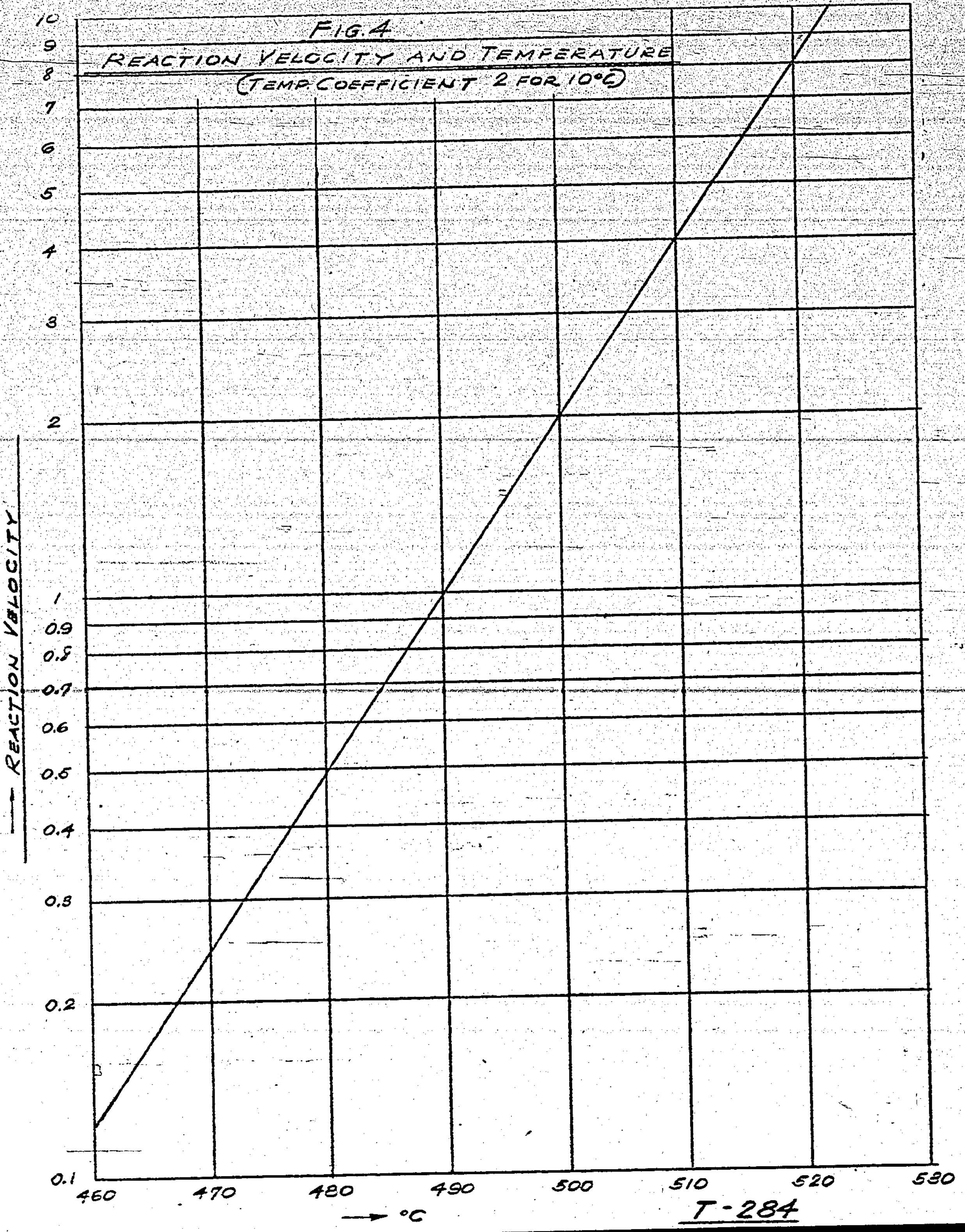
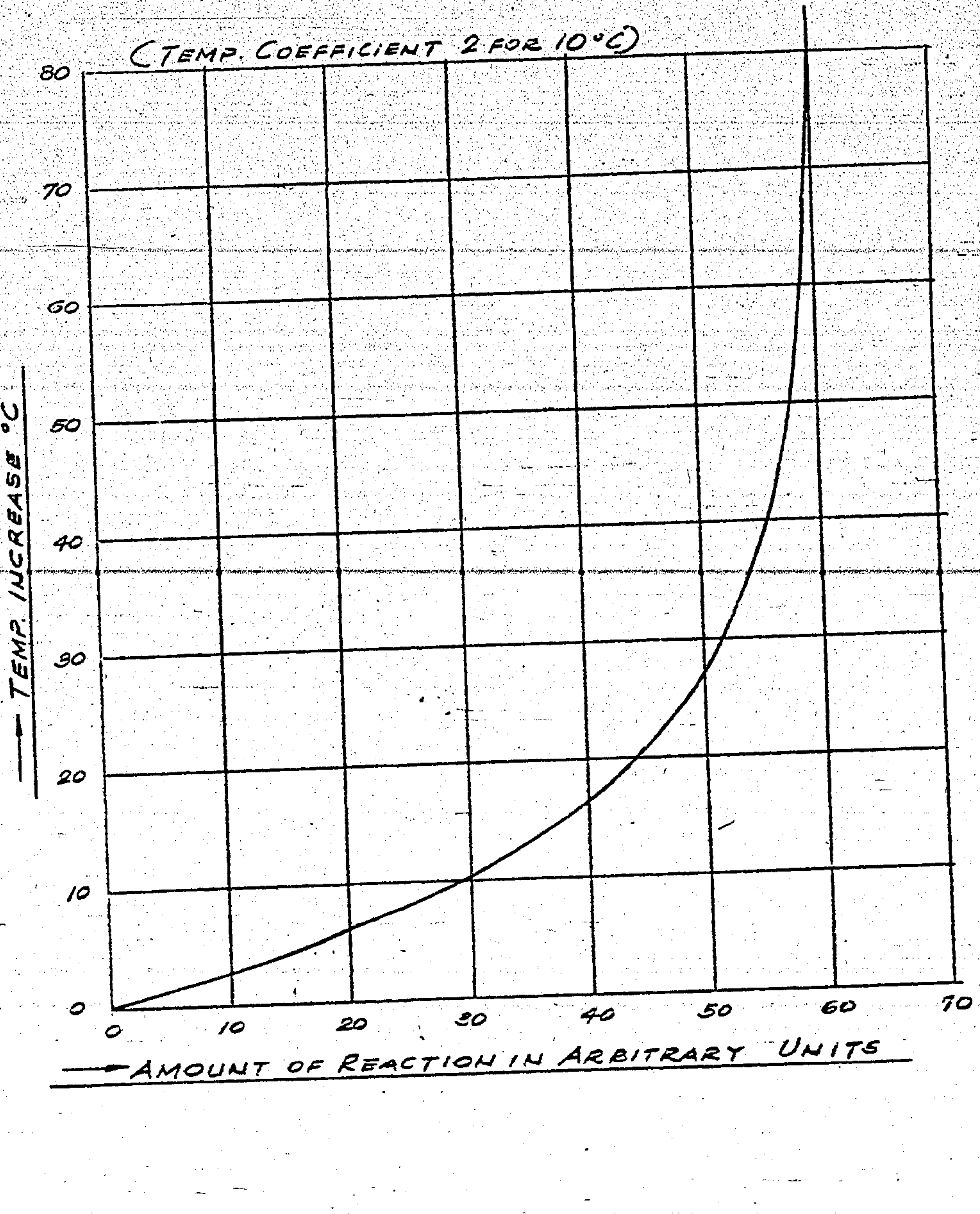


FIG. 4

REACTION VELOCITY AND TEMPERATURE

(TEMP. COEFFICIENT 2 FOR 10°C)

FIG. 5


(TEMP. COEFFICIENT 2 FOR 10°C)
TEMP. INCREASE °C
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
AMOUNT OF REACTION IN ARBITRARY UNITS

APPENDIX

Heat of Reaction and Temperature in Vapor Phase Stall

For a 7-bed, 24", vapor phase stall the following data were used for comparison with commercial vapor phase stalls in Germany. (For further details see Table I).

	7-bed 24" Conv.	Welheim	Gelsenberg Saturation	6434
Feed kg./l.h.	1.1	1.0	0.8	1.1
M^3 gas/kg.feed	3.2	2.5	4.0	2.0
Heat of reaction kcal./kg.feed	160	160	350	140
Temp. increase total °C./°F.	99/178	111/200	182/328	111/200
Average per bed °C./°F.	14/25	6-8/11-14	9-13/15-24	5-8/9-14
Length of cat. m	11	36-39	34-51	34-51
Velocity cm/sec. (empty converter)	5	12-13	28-42	18-28

These figures show that the total heat of reaction and, therefore, the total temperature increase during the reaction are well within the limits used in Germany in commercial operation. However, due to the small number of cooling gas introductions, the average temperature increase per catalyst bed is higher than in any other commercial stall. At the same time, the vapor velocity is smaller than elsewhere. That means that an operation at design thruput and gas rate will necessitate a very careful control of the reaction temperature, which is possible only with a large number of thermocouples.

To demonstrate where temperatures must be measured, see Figures 1 and 2. Figure 1 shows the distribution of the heat of reaction over the catalyst in a 300 atm. vapor phase stall. It can be assumed that a change of this curve for the 700 atm. operation will be small and without noticeable influence on the further conclusions. It may be seen that at equal temperature in the first of seven catalyst beds the heat of reaction is 26% of the total in comparison to 4% in the seventh bed. Using an equal average temperature of 490°C. in each bed, the calculation gives the temperature distribution as shown in Figure 2(a). According to the experience at Welheim, the danger of a runaway begins at about 502°C., this temperature being exceeded or reached in the first two catalyst beds. The average temperature in the catalyst beds can be increased from bed to bed as shown in Figure 2(b). Then a maximum temperature of 502°C. is not exceeded, but the maximum temperature in each bed is about 500-502°C., which means that a very careful control and measurement of all these temperatures is necessary. This is even worse if during the operation one of the catalyst beds (e.g. bed No. 1, Figure 2(c) loses its activity.

In Figure 3, the behavior of beds 1 and 4, Figure 2(a), and Figure 2(b), are shown in more detail. Furthermore, there are curves showing the change in the temperature gradient if the reaction temperature at the entrance of each bed is increased by 2°C. (broken) and 5°C. (dotted) respectively. These results are summarized in the following table.

	Temperature °C.	Rise in inlet °C.	Corresponding rise in outlet °C.
Temperature distribution as in Figure 2(a)			
Bed 1	477-503	2° - 5°	14° - 40°
Bed 4	484-497	5°	16°
Temperature distribution as in Figure 2(b)			
Bed 1	477-500	2° - 5°	8° - 26°
Bed 4	484-498	5°	18°

The data indicates that the first bed, Figure 2(a), is in danger of a runaway, whereas the fourth bed and beds 1 and 4, Figure 2(b), are tolerably stable against temperature changes at the inlet.

For the given design of this 7-bed vapor phase stall, the safety of the operation can be increased by an increase of the gas rate and/or by using a somewhat lower average temperature corresponding to a lower space time yield of gasoline.1/ This gives the following data.

1/ It may be remarked that the increase of the gas rate may raise to some extent the phenol and base content of the products.

Alternate Operations for 7-Bed 24" Converter

	Design	Higher gas rate	Smaller space time yield of gasoline
Feed kg./l.h.	1.1	1.1	1.1
M^3 gas/kg.feed	3.2	5.0	5.0
Gasoline kg./l.h.	0.41	0.41	0.35
Temperature increase:			
Total °C.	99	73	62
°F.	178	130	110
Temperature increase: (average per bed)			
°C.	14	10.5	9
°F.	29	19	16
Velocity in empty converter cm/sec.	5	8	8

The data for the temperature distribution and bed stability have been calculated for the actual bed size of the present Louisiana design and are presented in the first part of this report.

DISTRIBUTION OF THE HEAT OF REACTION IN 7 EQUAL CATALYST BEDS AT THE SAME TEMPERATURE

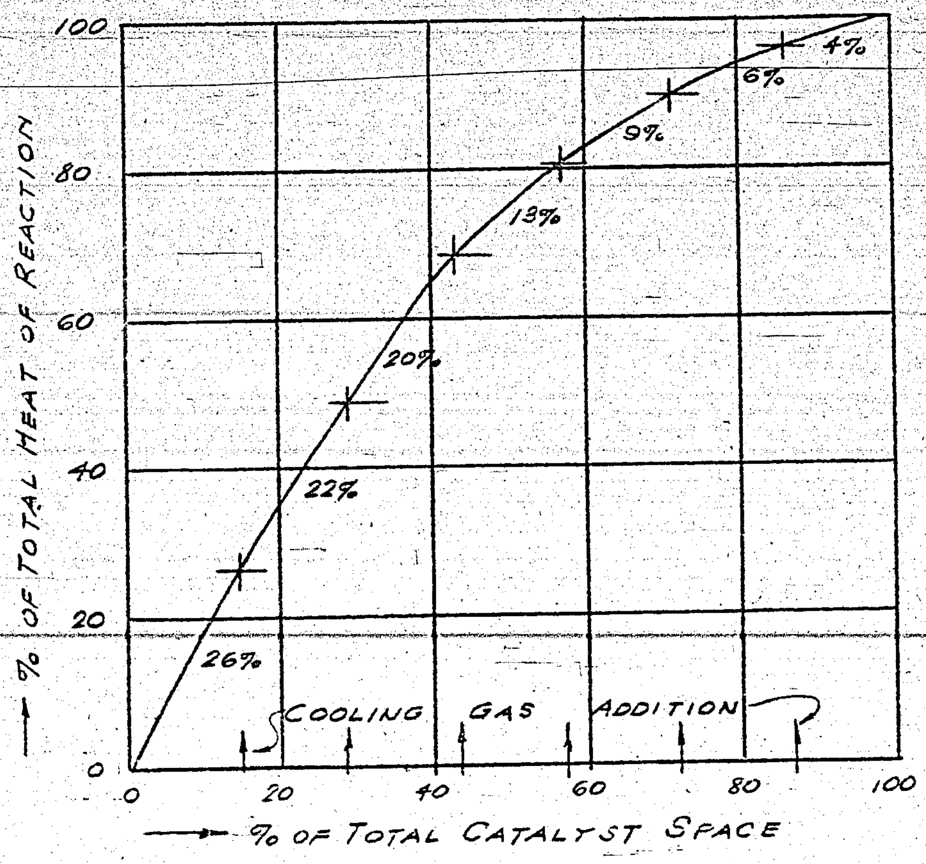


FIG. 1

APPENDIX

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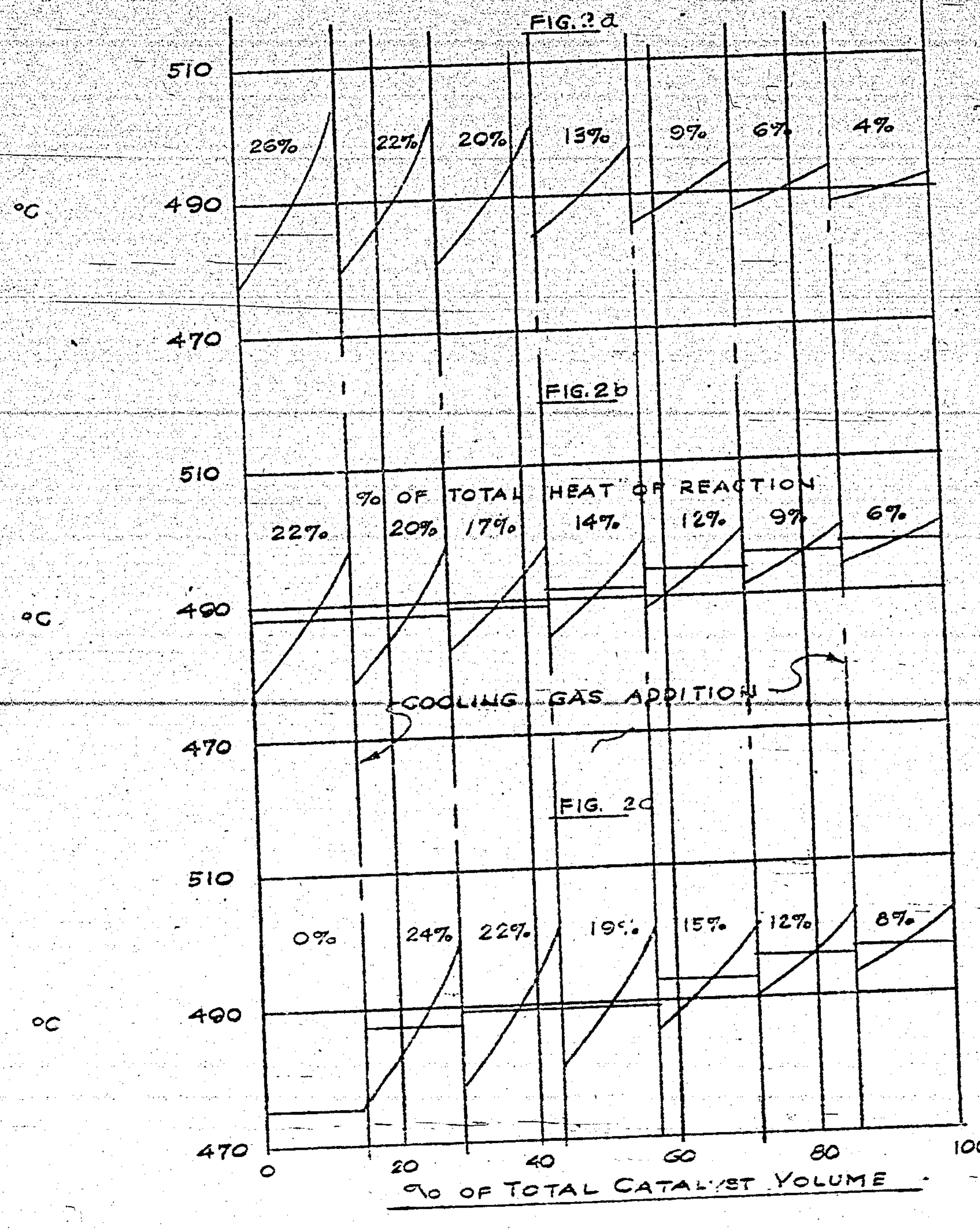
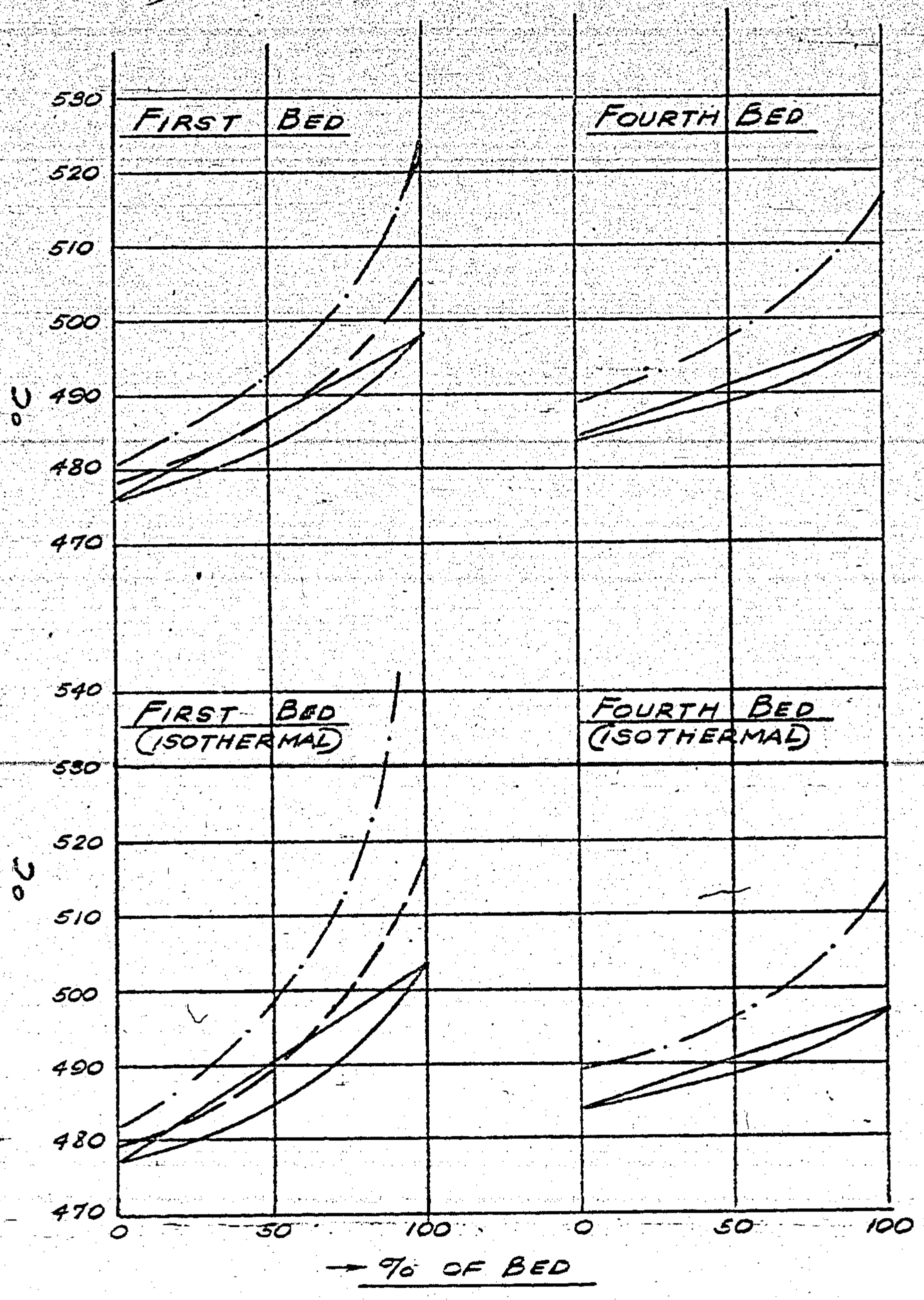
FIG. 2



(BASIS: DOUBLE REACTION VELOCITY AT 10°C HIGHER TEMP.)

FIG. 3


FIRST BED
FOURTH BED
FIRST BED (ISOTHERMAL)
FOURTH BED (ISOTHERMAL)
°C
530
520
510
500
490
480
470
°C
540
530
520
510
500
490
480
470
0
50
100
0
50
100
→ % OF BED

T-285
1/28/41

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

THE LINDE PROCESS.

Some basic principles are to be observed in the gas separation by the Linde principle:

1) Cold is produced by

   a) expansion with no production of work (Joule - Thomson effect)

   b) by expansion with the production of work (expansion machine)

   c) using additional refrigeration (evaporating ammonia, pre-evaporation of nitrogen under different pressures).

The Joule-Thomson effect is proportional to the pressure differences; it is therefore desirable to expand very greatly from a maximum pressure; and this the more so, as the work of compression increases entirely as the rise in pressure. The so-called Stockes' principle acts here unfavorably, according to which at higher pressures, exceeding say 25 atm., the densities of the compressed and the liquefied gas approach each other very closely, which causes difficulties in the separation of such gases. This throttling results in a great reduction in the heat content; i.e. as long as gases are in the superheated state, i.e. way above their saturation temperature, only cooling takes place. On the other hand, in the vicinity of the saturation point, there is only liquefaction.

Cooling by expansion, with the production of work, proceeds extraordinarily economically. It is, however, not readily accomplished in our case, with the C_1, C_2 and C_3 fractions present with the hydrogen, because expansion can only be carried out to the beginning of the liquefaction of these gases. The expansion process has therefore to be carried out in our case in several steps, with intervening liquefactions. This is however not economical.

II. One basic requirement which must be unconditionally adhered to, is as follows: all the components of the gases to be separated, which may be obtained in the solid form, must be completely removed before the start. For this reason, it is necessary to equip coke oven gas separation units with water and sodium hydroxide scrubbers, to remove all of the carbon dioxide. In our case a large water scrubber was necessitated by the need to remove acetylene, which is converted at -80° C to the solid state, by-passing the liquid state.

III. The supply of heat, required in the Linde installation for the distillation, is done by the introduction of fresh gas, which is cooled in the process. In principle, the total heat of the separated products is then transferred to the fresh gas input; the liquids separated will be re-evaporated. The condesing constituents will here be condensed at higher pressures, i.e. at higher temperatures, and separated. The liquefied gases are however to be evaporated mostly at lower pressures and therefore at lower temperatures.

IV. All losses of cold, unavoidable even with the best insulation, are compensated either at the temperatures at which they occur, or, better still, at still lower temperatures. For this purpose, auxiliary refrigeration installations are of particular value.

V. Before laying out the Hülse Linde installation, we have given careful consideration to using there the Linde-Fränkl method. Linde - Fränkl operates with recuperators, which are run to the plugging up, and are therefore built to alternate. This method of operation, which is particularly economical for the separation of air, would have had the very great disadvantage in our case, of requiring a large number of intermediate fractionations with the alternating process. Such a Linde - Fränkl installation may be best compared with a producer, in which large amounts of gas were to be discarded for the purpose of obtaining pure gas fractions.

W. M. Sternberg

C. H. Patents

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T-286

KCBraun
3/25/47

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR MAKING GOOD ANTI-KNOCK GASOLINES

German Patent 729043
Class 12o, Group 105,
22 Nov. 1936

Issued To

I. G. Farbenindustrie A.G.
Frankfurt A. M.

By

Dr. Heinrich Bütefisch, Leuna, Kr. Merseburg,
Dr. Karl Winkler, Bottrop-Boy, and
Dr. Hermann Kaufmann, Leuna, Kr. Merseburg.

DRP 729043

In the pressure hydrogenation of bituminous coal, or extracts or tars of bituminous coal, or high boiling constituents thereof, a certain amount of gasoline is produced in the liquid phase, which is rich in phenols and strongly unsaturated compounds, of which it can be freed only with great loss by the usual refining methods. It is, therefore, customary to subject this gasoline, together with the higher boiling products, to pressure hydrogenation in the vapor phase, wherein, however, appreciable losses are also caused by the formation of gas.

It has now been discovered that a product of exceptionally good properties is obtained from said gasoline, if it is subjected to pressure hydrogenation, in which splitting is avoided, if at all possible. For this purpose it is heated, together with H_2 at a pressure of about 30 to 60 atm and a partial pressure of the gasoline between about 0.5 and 3 atm, to temperatures between about 460 and 510° C in the presence of suitable catalysts with a splitting effect as low as possible. Particularly suitable as such are, e.g. nickel-tungsten catalysts, particularly those containing both metals as sulfides, as well as catalysts containing other sulfides or oxides of the metals of the fifth or sixth group of the periodic system, or both groups by themselves or mixed with sulfides or oxides of heavy metals of the first or eighth group, or both groups. The catalysts may further contain additions of non-reducible oxides, such as zircon, thorium or cerium oxide, as well as other additions, or be applied on carriers.

When the gasoline is treated in the manner described, a partial or complete saturation of strongly unsaturated hydrocarbons, as well as a reduction in phenols, will occur simultaneously with pressure hydrogenation, and a product is obtained whose properties meet the demands of the market and which has a high anti-knock value besides. Octane numbers of 90 and above may be obtained in this manner, so that the gasoline may even be directly used for special purposes, such as aircraft. The products are also readily miscible with ethyl and methyl alcohol and can, therefore, also be used to improve gasolines with less satisfactory properties.

For example, the process is conducted so that bituminous coal or bituminous coal extract is mixed with a high boiling substance, such as the liquid residue from pressure hydrogenation, or that tars or high boiling bituminous coal tars or residues are directly hydrogenated under pressure in the liquid phase, and the vaporous products are separated from the residues and condensed. The low boiling (to about 200°C) constituents of the product are passed over a nickel-tungsten catalyst at about 480°C and an H_2 pressure of 50 atm with a partial pressure of the gasoline of 0.5 to 3 atm, whereby only a very small quantity, not exceeding a few percent, is transformed into gaseous hydrocarbons. The gasoline so treated possesses the superiorqualities above described.

Example.

From 100 parts of extract, 30 parts of a gasoline boiling to 200°C with a spec. gravity of 0.880, besides fuel oil, are obtained by pressure hydrogenation of bituminous coal extract at 300 atm and about 480°C. The gasoline is passed over a catalyst compressed into solid pieces and consisting of two parts tungsten-sulfide and one part nickel-sulfide, together with H_2 at a pressure of 50 atm and 475°C. The proportion of gasoline to H_2 equals one liter gasoline (liquid) to 5000 liter H_2.

While the freshly distilled feed gasoline will assume a dark color within a few hours, the gasoline obtained after treatment remains entirely clear and colorless. It contains 60% aromatic hydrocarbon and has an octane number of 90. The foul smell has completely disappeared. The tests equal those of a good commercial gasoline.

Although it is known (compare French patent 749843) that pressure hydrogenation gasolines of any kind may be subjected first to a refining and subsequently to a dehydrogenating H_2 treatment, this process did not offer the direct possibility of combining the two hydrogen treatments into one operation.

Patent Claim.

Process for making good anti-knock gasolines from bituminous coal, bituminous coal extracts, bituminous coal tars or high boiling constituents of bituminous coal tar, by pressure hydrogenation and subsequent dehydrogenation at moderately high H_2-pressure and low partial pressure of the gasoline, avoiding splitting, if at all possible, characterized by separating the gasoline obtained by pressure hydrogenation of said substances in the liquid phase, and dehydrogenating it at temperatures between about 460 and 510°C and pressures of about 30 to 50 atm with a partial pressure of the gasoline of about 0.5 to 3 atm.

C.H. Patents

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T-287

KCBraun
3/25/47

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR THE PRESSURE HYDROGENATION OF SOLID FUELS.

German Patent 729490
Class 12o, Group 1o5,
22 Dec. 1938

Issued to

I. G. Farbenindustrie, A. G.
Frankfurt a. M.

By

Dr. Mathias Pier, Heidelberg
Dr. Kur Peters, Ludwigshafen, Rh., and
Dr. Wolfgang Jäckh, Heidelberg

DRP 729490

It was known that in the pressure hydrogenation of asphaltic oils or of substances forming asphalt or resin in a thermal treatment, such as coal, care must be taken that the oils introduced into the reaction vessel with the feed materials are not so H_2-rich that they will cause a separation of asphalt or resin. It has, therefore, already been proposed to free the feed materials of low boiling aliphatic constituents, as well as of paraffin, before introducing them into the pressure hydrogenation vessel, or to use H_2-poor oils, such as tar oils or pressure hydrogenation residues for pasting asphalt producing substances. However, these pasting oils have this disadvantage, that they contain substances obtained in their production by distillation, which lead to the formation of undesirable, high molecular substances in the pressure hydrogenation vessel and so disturb operations.

It has now been found that solid, possibly meltable, carbonaceous fuels may be hydrogenated under pressure without trouble, if a pasting oil is used which has been obtained from the residues of the pressure hydrogenation of such substances by mixing them with saturated hydrocarbons, normally liquid, possibly under pressure, at such a high temperature that practically everything will dissolve. In certain cases the solution obtained may be freed of solid constituents and decomposed into H_2-rich and H_2-poor constituents by cooling to a temperature at which two layers are formed but no asphalt is yet precipitated, or with the aid of selected solvents or a combination of both methods.

Using a pasting oil so obtained has these further advantages, that pressure hydrogenation may be conducted at a temperature about 10°C lower than when using the known pasting oils, such as tar oils, without a deterioration of the coal conversion, and that about 20 to 30% less gaseous hydrocarbons are formed.

The pasting oils produced according to this invention are also superior to H_2-poor oils obtained from pressure hydrogenation residues by dehydrogenation already proposed, inasmuch as they make it possible to obtain better conversion and superior products.

Suitable feed substances are coal, peat, wood, concentrated sulfite waste liquor, pitch, asphalt, resin or pressure extracts of these substances. Except for meltable substances, these are reduced to small particles, pasted with a suitable oil in the proportion 1:1 or 1:2, and hydrogenated at pressures of 100 to 1000 atm and temperatures between about 300 to 550°C.

The separation of the H_2-rich oils may be combined in a simple manner with the processing of the products of pressure hydrogenation. It was surprising that not only the solid constituents, whose removal from residues of pressure hydrogenation has herebefore caused considerable difficulties, could be removed in a simple manner, but that an extensive decomposition of the high boiling pressure hydrogenation products into H_2-poor and H_2-rich oils also takes place.

The following method illustrates the procedure:

The pressure hydrogenation product is split in separating vessels maintained at suitable temperatures or by fractionating condensation so that an oil mixture, suitable, within its boiling range, for pasting fresh feed materials, is obtained. This mixture is mixed at temperatures of over 100°C, e.g. 200 to 350°C, possibly under pressure, with an H_2-rich hydrocarbon, e.g. a low boiling product obtained in the conversion of CO by H_2, or a mixture of hydrocarbons produced by pressure hydrogenation in the vapor phase under strongly hydrogenating conditions, or a hydrogenated cyclical compound, such as deca-hydronaphthalene, or some other H_2-rich hydrocarbon, then filtered or centrifuged. The oil free of solids obtained hereby is cooled to such an extent that two layers are formed, care being taken that the temperature does not drop so low that asphalt is precipitated. The formation of the layers may be effected by the addition of a low molecular hydrocarbon, such as methane, ethane or propane, or some other selective solvent, e.g. liquid sulfur-dioxide, instead of or simultaneously with the cooling.

On the one hand, we obtain a mixture of H_2-rich hydrocarbons, which may be processed to gasoline, diesel oil, illuminating or lubricating oil, and an H_2-poor oil, which, when used as pasting oil, will prevent all trouble herebefore experienced, on the other.

Example.

A sludge (letdown) obtained in the pressure hydrogenation of bituminous coal with 18% constituents insoluble in benzol is mixed with heptane at about 220°C in the proportion 1:1 and filtered under pressure. About half the quantity of liquid sulfur-dioxide is added to the still hot filtrate. The mixture is then slowly cooled, forming two layers in the process. The lower layer contains the sulfur-dioxide with the dissolved H_2-poor constituents, which are used as pasting oil for coal after separating the sulfur-dioxide. The upper layer consists of H_2-rich hydrocarbons, from which the heptane can be easily separated.

If, instead of using the H_2-poor oil so obtained as pasting oil in the pressure hydrogenation of the same coal, an oil obtained by known methods by dehydrogenation at 700°C of a mixture of the sludge recovered in centrifuging the residue obtained in pressure hydrogenation and of heavy oil, is used together with the oil obtained in centrifuging, the yield in oil and asphalt is reduced by about 20%. The coal conversion deteriorates and the heavy oil obtained contains about twice as much asphalt and substances insoluble in benzol as when working according to this invention.

Patent Claim.

Process for the pressure hydrogenation of solid, possibly meltable, carbonaceous fuels pasted with an H_2-poor oil recovered from pressure hydrogenation residues of said substances, characterized by using an H_2-poor pasting oil obtained by mixing the said pressure hydrogenation residues with saturated, normally liquid, hydrocarbons, possibly under pressure, at such high temperatures that practically everything is dissolved, possibly removing the solid constituents from the solution so obtained and splitting the solution so obtained into H_2-rich and H_2-poor constituents by cooling to a temperature at which two layers are formed but no asphalt is yet precipitated, or with the aid of selective solvents, or by both methods.

C.H. Patents

568 T-288

KCBraun
3/26/47

U.S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR THE CONTINUOUS PRESSURE HYDROGENATION OF SOLID, NON-MELTABLE CARBONACEOUS SUBSTANCES.

German Patent 725603
Class 12o, Group $1o_5$,
31. July, 1937

Issued to

I.A. Farbenindustrie A.G.
Frankfurt a. M.

By

Dr. Mathias Pier, Heidelberg, and
Dr. Walter Kronig, Ludwigshafen, Rh.

DRP 725603

In the continuous pressure hydrogenation of solid, non-meltable, carbonaceous substances, such as coal, oil shale or peat, in a pasted condition, it has been found especially advantageous to heat the reaction material, together with H_2, close to the reaction temperature under pressure, then keep it at approximately the same temperature without decompression in a pressure vessel with a capacity about 20 to 40% of the reaction space proper, and then convey it to the reaction vessel after its temperature has been increased to that necessary for reaction. This operating method is particularly suitable for coal with a carbon content above 84%.

In the new process for example, the feed materials, together with H_2, with or without the addition of catalysts, are heated in a pipe coil, which may be part of a heat exchanger, at a pressure essentially equal to the reaction pressure, to a temperature of about 300°C, preferably between 340 and 440°C, and then conveyed to an intermediate vessel of the above mentioned capacity, in which they are kept for a time without appreciable decompression at the same temperature or one not deviating from it by more than 40°C, without, however, quite reaching the desired reaction temperature. It is then conveyed to a second preheater, which may also be a pipe coil, possibly with further additions of H_2 and catalyst, where it is heated to the reaction temperature. The inside volume of the two pipe coils and the intermediate vessel combined should equal about up to 60%, and of the second heating coil alone about 5 to 10%, of the reaction space.

The use of an intermediate vessel of this size, instead of a larger vessel, has this advantage, that, while coarse particles, which would cause trouble in the reaction vessel, may be settled out or more uniformly distributed, particles necessary for conversion, e.g. catalyst and coal particles, are not separated and no separation of hydrogenation gas and coal paste takes place. A small intermediate vessel has the further advantage of savings in the cost of expensive high pressure vessels.

Pressure hydrogenation is conducted at temperatures above 460°C, properly above 470°C, with the usual pressures between 50 and over 600 atm. The thru-put when using coal is 0.4 kg or more per liter reaction space per hour. The residence time in the intermediate vessel, whose size is known, can be obtained directly from the thruput.

The reaction is properly conducted in the presence of catalysts suitable for pressure hydrogenation, e.g. metals of the fifth to the eighth group of the periodic system or their compounds, particularly sulfides or oxides of heavy metals, possibly together with halogens or metalloid-halogenides. Tin and its compounds are also well suited as catalysts. The use of carriers, such as brown coal Grude (coke) active coal or fuller's earth, which may be treated with hydro-fluoric acid, is advantageous in many cases.

The products are split into vaporous substances going off with the hydrogen, and liquid substances containing the solid constituents, in a catch pot. From the vaporous products, anti-knock gasolines and higher boiling oils, suitable for diesel or fuel oil, may be recovered. The products drawn off in liquid form can be processed to fuel oil by further hydrogenation, possibly at higher pressure.

In the pressure hydrogenation of coals, tars or mineral oils, it is, in fact, well known to heat the feed materials to the reaction temperature gradually, without interrupting the temperature rise, with decreasing heat supply towards the end of the heating period. The process at hand differs therefrom in principle, inasmuch as the gradual rise in temperature is interrupted by the introduction of an intermediate vessel. Only then is the temperature increased to the reaction temperature.

Example.

A bituminous coal containing 85% C is pasted with an oil obtained in the pressure hydrogenation of the same coal and consisting of 30 parts middle oil and 70 parts heavy oil. This mixture is mixed with 0.06% tin oxalate and 1.15% ammonium chloride (based on the coal) and conveyed to hydrogenation, together with 0.5 parts (based on 1 part coal used) of a product obtained by pressure hydrogenation of the same coal and withdrawn in liquid form from the catchpot. The mixture is first heated to 425°C, in a heating coil holding 120 liter, at an H_2-pressure of 250 atm. It is then conveyed at the same pressure thru the bottom of an intermediate vessel holding about 1 m^3 and kept at this temperature during its flow thru the vessel. The mixture is then conveyed from the upper part of the vessel into a second pipe coil holding 80 liter, is there heated to 480°C, and then conveyed to reaction vessel holding about 3 m^3. The thruput herein is 0.75 kg coal per liter reaction space per hour. The splitting of products of reaction takes place in a hot catchpot connected to the reaction vessel and kept at a temperature of about 460°C.

The coal is converted 94% in this operating method. The oil obtained consists of 25% gasoline, which has an octane number of 81 after cleaning, and 75% higher boiling oil, which can be used as fuel oil. A portion of the product withdrawn from the catchpot in liquid form (Abschlamm or letdown), together with middle and heavy oil obtained by condensation from the vaporous products, is used for pasting fresh coal. This pasting oil contains about 13% asphalt.

If the coal is heated to reaction temperature in a pipe coil of the herebefore usual content (about 8% of the reaction space), a coal conversion of only 88% is obtained, and the pasting oil recovered from the products of reaction under otherwise equal conditions contains 18% asphalt.

Patent Claim.

Process for the continuous pressure hydrogenation of solid, non-meltable, carbonaceous substances, such as coal, oil shale or peat, in pasted condition, characterized by heating the reaction material under pressure, together with H_2, to close to the reaction temperature, at which temperature it is kept without decompression in a pressure vessel holding about 20 to 40% of the reaction space proper, and then conveying it into the reaction vessel after its temperature has been raised to that necessary for reaction.

C H Patents

570

T-289

KCBraun
3/26/47

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

PROCESS FOR SPLITTING OR PRESSURE HYDROGENATION OF CARBONACEOUS FUELS

German Patent 725604
Class 12o, Group 105,
6. April, 1940

Issued To

I. A. Farbenindustrie A.G.
Frankfurt, a. M.

By

Dr. Eugen Anthes, Ludwigshafen, Rh.
Dr. Wilhelm V. Füner, Ludwigshafen, Rh.
Dr. Walter Simon , Ludwigshafen,Rh.

DRP 725604

It is known that splitting or pressure hydrogenation of carbonaceous substances may be conducted in the presence of catalysts consisting of mixtures of metallic sulfides obtained by heating dry mixtures of ammonium-sulfo-salts containing metals of the sixth group of the periodic system in the residual acid and other substances acting as carriers or catalysts. Catalysts produced by decomposition of metallic carbonyls in the presence of carriers have also been used in these reactions.

It has been found that especially favorable results may be obtained with the said processes, if catalysts are used, which have been obtained by heating dry mixtures of ammonium-sulfo-salts containing metals of the sixth group of the periodic system in the residual acid with finely distributed metals of the iron group obtained from the corresponding carbonyl compounds, to temperatures above 300°C.

For the production of the catalyst, the compounds of metals of the sixth group given preference are ammonium-sulfo-molybdate or wolframate, which, e.g. can be produced by dissolving molybdic or tungstic acid in an ammonium-sulfide solution with the introduction of hydrogen sulfide. The sulfo-salts, so obtained are then mixed with iron Nickel or cobalt produced in finely divided form by decomposition of the corresponding carbonyl in a heated chamber in a characteristic manner, wherein the metals of the iron group are used in quantities ranging between 1 and 50%, particularly 5 to 25%.

The dry mixture of sulfo-salt and metal is now heated to temperatures of 300 to 500°C, preferably 375 to 475°C, for sometime, e. g. 1 to 24 hours, possibly after first grinding it. As a rule, this is done in a gas stream containing H_2, CO_2 or N_2, or several of these gases. The effectiveness of the catalyst is increased, if a sulfuring medium, like H_2S, is added during heating.

Example.

Nickel, produced by thermal decomposition of nickel-carbonyl, is thoroughly mixed ina ball mill with ammonium sulfo-wolframate in the molecular proportion 1:2 and treated in a hydrogen stream at 400 to 450°C for 2 to 3 hours, until the formation of ammonia has ceased. The powder is cooled in a hydrogen stream and shaped.

A gasoline, obtained in the pressure hydrogenation of bituminous coal, with a boiling end point of 185°C and a content of aromatic hydrocarbons of 7%, is passed over this catalyst in vapor form, together with H_2, at a pressure of 50 atm and a temperature of 485°C. The thruput selected herein is 0.5 kg feed material per liter catalyst space per hour and an H_2-volume of 2 m^3 per kg feed material per hour. The gasoline obtained contains 57% aromatic hydrocarbons.

If a catalyst is used, which has been produced by heating a mixture of ammonium-sulfo-wolframate and nickel-chloride in a hydrogen stream to 450°C, and which contains tungsten and nickel in the same proportion as the above catalyst, a gasoline containing only 49% aromatic hydrocarbons is obtained under otherwise equal conditions.

When using a catalyst of the same composition, which has been produced by heating to 450°C a mixture of tungsten and nickel powder, obtained from the corresponding carbonyls, first by passing H_2S over it and then in an H_2-stream, and shaping it, a gasoline containing only 51% aromatic hydrocarbons is obtained under otherwise equal conditions.

Patent Claims.

Process for splitting or pressure hydrogenation of carbonaceous fuels in the presence of metallic sulfide mixtures produced by heating mixtures of ammonium-sulfo-salts, which have been produced in a dry state and contain metals of the sixth group of the periodic system in the residual acid, and other catalytically acting substances, to temperatures above 300°C, characterized by using sulfide mixtures, for the composition of which finely distributed metals of the iron group, obtained from the carbonyls, besides ammonium-sulfo-salts, were used.

C.H. Equipment

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-290
573 W.M. Sternberg

High Pressure Experiments
Leuna 558

April 6, 1947

TUBULAR CONVERTERS

From Dr. Pier's private files.

The frictional resistance to flow of one single hairpin of a tubular converter was measured with uncompressed nitrogen. The amounts were measured with a 15 mm orifice. The frictional resistance to flow of the connecting hose was

with 840 565 430 360 mm oil column differential pressure at orifice

$w =$ 70 50 40 35 mm water column.

Frictions inside the different hairpins are practically the same. They amount

with 730 mm oil column with a 15 mm orifice

i.e. with 39 m^3/hr

$W =$ 270 mm Hg.

With the volume passing thru the hairpin, the resistance of the connecting hose is $w = 62$ mm water column $= 4.56$ mm Hg. The resistance to flow of a hairpin is accordingly

$$W - w = 270 - 4.5 = 265.5 \text{ mm Hg.}$$

The Reynolds number is therefore

$$R_e = \frac{0.036 \times 39 \times 1.15 \times d_k}{160^2 \times 1.8 \times 10^{-6}} = 80 \times d_k$$

The coefficient of resistance C

$$C = \frac{265.5 \times 13.6 \times 6.58 \times 10^8 d_k}{2.21 \times 10^4 \times 1.15 \times 79.5 \times 10^2 \times 12 \times 280} = 3.5\ d_k$$

where d_k is the average diameter of the catalyst pills. This gives us the apparent diameter of the spheres of the catalyst filling as

$d_k =$ 9 10 mm

$R_e =$ 720 800

$C_1 =$ 31.5 35

On the other hand, we get from the expression $C_2 = 94 R_e^{0.16}$

$$C_2 = 33 \quad 32$$

The apparent diameter of spheres is between 9 and 10 mm, and we get by interpolation $d_K = 9.33$ mm.

The resistance to flow inside the tubular converter is computed using this value. It is based on the arrangement of four (4) lines being connected in parallel, with every 2 hairpins in series.

The thruput in feed and gas is supposed to be

	7,600 kg feed with M = 100	corresp. to	$\frac{7600 \times 24}{100}$	=	1820 m³/h
and	2,100 kg gas, $s_n = 0.35$ kg/m³	" "	$\frac{2100}{0.35}$	=	6000 m³/h
Total	9,700 kg	Total Volume			7820 m³/h

$$\text{Average sp. gr. } \frac{9700}{7820} = 1.24 \text{ kg/m}^3$$

The average pressure in the tubular converter is assumed to be 50 atm.

The average temperature is 25 mv. = 476° C = 749° K.

1) <u>Tubular Converter in Series with Other Converters:</u>

Amount of gas per line: $Q = \frac{7820}{4} = 1955$ m³/h

The Reynolds number becomes then

$$R_e = \frac{0.036 \times 1955 \times 1.47 \times 9.3}{2.56 \times 10^4 \times 2 \times 10^{-6}} = 15.9 \times 10^3$$

The value of the coefficient of resistance for a Reynolds number = 15,900 is 20.

and the resistance of two hairpins connected in series is

$$\frac{2.21 \times 10^4 \times 20 \times 1955^2 \times 24 \times 749 \times 1.24}{9.3 \times 51 \times 160^4} = 12 \times 10^4 \text{ mm water column}$$

$$= 12 \cdot 1 \text{ atm.}^*$$

Results of computation agree with the earlier assumed value of 12 atm for the total amount assumed at that time of 9500 m³/h (7700 m³ gas, 7500 kg/h feed.

2). <u>Tubular Converter Parallel with Converter I</u>

If the tubular converter is arranged in parallel with the converter I and the feed and the amount of gas is distributed among the two converters in

---

* This will cause the whole coefficient to increase to 48 ... 50 atm.

proportion to their reaction spaces, the thruput thru the tubular converter will be

$$Q = 0.407 \times \frac{7820}{4} = 795\ m^3/h$$

The Reynolds number will then be

$$R_e = \frac{0.036 \times 795 \times 1.24 \times 9.3}{160^2 \times 2 \times 10^{-6}} = 6.45 \times 10^3$$

and the coefficient of resistance C = .22, while the drop in pressure

$$\frac{2.21 \times 10^4 \times 22 \times 795^2 \times 24 \times 749 \times 1.24}{9.3 \times 51 \times 160^4} = 2.2 \times 10^4 \text{ mm water column,}$$

$$= 2.2 \pm 0.2 \text{ atm}$$

According to measurements taken during operation, the drop in pressure in converter I is 0.9 atm with 4600 m^3/h of gas and 6536 kg/h feed, giving a total volume of 6170 m^3/h, with a density of 1.32 kg/m^3.

The parallel connection of the tubular converter with converter I does not produce any changes in the distribution of flow, and a correct proportioning of the gas between the converters is produced by throttling down the inlet into converter I. The other drops in pressure in the stall will be approximately in the proportion

$$\frac{(7820)^2}{(6170)^2} = 1.6,$$

and the difference for the stall, exclusive of the converter I must be about 21 x 1.6 = 34. The total stall difference will accordingly be 34 + 2 = 36.

3). <u>Tubular Converter in Parallel with Converters I - IV.</u>

The thruput through the tubular converter was 1.5 to/m^3 in the computations above.

Should one reduce the thruput of 0.5 to/m^3, the amount injected into the tubular converter would be 1000 kg feed and 800 m^3 of gas, or a total amount 1040 m^3/h with an average specific gravity of 1.24. The total amount per line would be

$$\frac{1040}{4} = 260\ m^3/h.$$

The branch stream of the tubular converter is supposed to combine with the main stream back of converter IV. The throttling will have to be done ahead of the tubular converter and the pressure in the tubular converter would correspond to the stall pressure between the converter IV and return pass of the heat exchanger I. Assuming an outlet pressure of 22 atm this pressure should be 22 + 4 x 1.6 = 28.4 atm.

The average pressure in the tubular converter is 29 atm.

The Reynolds number will then become

$$R_e = \frac{0.036 \times 260 \times 1.24 \times 9.3}{160^2 \times 2 \times 10^{-6}} = 2.11 \times 10^3$$

The coefficient of resistance is 28.

The drop in pressure will be

$$\frac{2.21 \times 104 \times 28 \times 1.24 \times 260^2 \times 24 \times 749}{9.3 \times 30 \times 6.58 \times 10^8} = 5.1 \times 10^3, \text{ or}$$

0.5 -- 0.6 at.

The drop in pressure in the last part of the stall between the return pass of the heat exchanger I and to the stage cooler outlet will increase from 4 atm to about 4 x 1.6 atm = 6.4 atm. The stall difference will thus be increased by only about 2.5 atm through a parallel connection of the tubular converter. There will have to be a pressure drop of about 17 atm at the hot regulating valve of the tubular converter.

SUMMARY

1). The tubular converter is connected in series with the other converters.

7600 kg/h feed; 6000 m^3/h gas, s_n = 0.35 kg/m^3

Drop in pressure = 12 ± 1 atm; Stall difference* - 48 -- 50 atm.

2). Tubular converter in parallel to converter I.

~~Throughput through tubular converter 3100 kg/h feed; 2450 m^3/h gas~~

Drop in pressure = 2.2 ± 0.2 atm. Stall difference * about 36 atm.

3). Tubular converter parallel to converter I to IV incl.

Thruput through tubular converter: 1000 kg/h feed; 800 m^3/h gas, correspond to 0.5 te/m^3; Drop in pressure = 0.5 -- 0.6 atm; stall difference * att. 24.5 atm.

Signed: Hamacher

* The values for the stall differences are based on measurements of 3/27/43

/pkl

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-291
W.M. Sternberg

TRANSLATION OF A MANUSCRIPT SUPPLIED BY DR. FRESE

"KONTAKTFABRIK BAU 53 KONTAKT ZUSAMMENSETZUNG"

"CATALYST PRODUCTION BUILDING 53 COMPOSITION OF CATALYSTS".

Ruhröl G.m.b.H   Bottrop, May 23, 1945

Dr. Dö/Ha

Copy. (In pencil: Collected for an American Committee of 4 persons, May 22, 1945)

An example for the Preparation of the Welheim Gas Phase Catalyst.

(Summarized for an American Commission of four persons, May 22, 1945; draft submitted 8/23 to two American members of C.J.O.S.)

Directions for the preparation of 60 kg of the finished catalyst.

Required:

90 kg	AD5 paste with an average water content of 60%, 36kg dry substance
24 kg	Terrana
4.1 kg	hydrofluoric acid, HF (70 - 72%)
3.7 kg	ZnO
3.0 kg	sulfur, S (as flowers of sulfur)
2.3 kg	Chromic anhydride, CrO_3
1.4 kg	ammonium sulfomolybdate $(NH_4)_2MoS_4$
16 kg	aqua ammonia (d= 0.910)

<u>Preparation</u>: 90 kg of the AD5 paste are kneaded in a kneading machine for a half hour with the addition of 4.1 kg hydrofluoric acid. 10 kg of terranna is added and the mixture kneaded for an additional 10 minutes. About 3.7 kg zinc oxide, 3.0 kg. sulfur and 2.3 kg chromic anhydride (in the form of 50% water solution are added next and the mixture kneaded for ten additional minutes for a proper homogenization. An additional 10 kg terrana are added next and the acid mixture neutralized by the addition of about 9 kg technical grade aqua ammonia. In conclusion, 1.4 kg ammonium sulfomolybdate dissolved in 7 kg ammonia are added, as well as the rest of the terrana, and the mixture well kneaded for about 20 minutes longer. The catalyst mass now is pressed in catalyst presses into pills 10 mm in diameter and dried for 3 - 4 days in a drying oven at 70 - 75°. In conclusion, the pills are activated in a stream of hydrogen at 350 - 360° C for twelve hours.

/s/ Döring

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PRELIMINARY TESTS:

1) G 18 with K 320:
(Stall II)
5/8 - 6/10, 1940.

100% A.D.V. paste
9.3 g. HF / 100g carrier
2% Cr) ammoniacal
1% Mo)
2% Fe, as precipitated Fe(OH)$_3$

2) G 19 with K 331:
(Stall I)
5/22 - ~~6/18,~~ 1940

60% A.D.V.
40% Terrana
3.1 g HF / 100 g carrier
1% Cr) ammoniacal
1% Mo)
2% Fe, as precipit~~ated Fe~~(OH)$_3$

3) G 20 with K 343:
(Stall II)
6/13 - 6/21, 1940

60% A.D.V.
40% Terrana
20 g HF / 100 g carrier
2% Cr, acid
1% Mo ammoniacal
2% Fe as Fe(OH)$_3$, Merck

4) G 21 with K 345:
(Stall I)
6/26 - 1940

60% A.D.V.
40% Terrana
3 g HF / 100 g carrier
2% Cr, acid
1% Mo, ammoniacal
2% Fe as Fe(OH)$_3$, Merck

Date of preparation: June 24 - July 23, 1943.

Total production:				
	12 mm pills	3,927 kg	=	5.97 m^3
	10 mm pills	1,194 "	=	1.81 "
	Total	5,121 "	=	7.78 "

Composition:
60% A.D.V. paste (60% H$_2$O)
40% terrana, extra
5 g HF/100 g carrier.
2% Fe as hydroxide
2% Cr as CrO$_3$, acid
1% Mo as the sulfosalt, ammoniacal.

Raw materials:
1). A.D.V. paste: Ver. Bleicherde Fabr. Munich
45% from shipment of 2/16/40 frozen
55% " " 6/13/40 normal

2). Terrana, extra: Ditto
Drawn from storage, Bldg. 29
H$_2$O - free

3). Hydrofluoric acid, techn. grade; I.G.Farbenindustrie, Leverkusen, 70 - 75%
HF, determined: 72.6%
D^{20} about 1.13
shipment of June 19, 1940

4). Iron hydroxide, techn grade, powdered; Merck
Catal. 3355
Iron content found 59.4%

5). Chromic anhydride techn grade, 99%, crystallized, Merck
CrO_3, by analysis 98.4%
Cr, " " 51.2%
Used in 40% solution.

6). Ammonium sulfomolybdate, 98-99%; Riedel d. De Haen,
Mo content, from analysis 30.4%
used as 20% solution in ammonia, sp.gr. 0.910

7). Ammonia water, technically pure, 0.910
Bros Overlack, M.-Gladbach -
NH_3 contents, from table. 25%

Compounding: 60 kg dry batch

Filling: 90 kg A.D.T. (dry 36.0 kg)
Added: 2 kg $Fe(OH)_3$ (" 2.0 ")

Mixed 5 minutes

Added: 4.1 kg hydrofluoric acid
1 kg water
5 - 6 kg Terrana (dry 6 kg)

Mixed 30 minutes

Added: 6 kg chromic acid solution (2.4 kg solid)
2 liters water
abt. 15 kg terrana (dry 15 kg)

Mixed 10 minutes

Added next: 6 kg ammonia water
3 liters water

Mixed 10 minutes

Added next: 2 kg ammonium sulfomolybdate in solution in
9 kg ammonia water (2)
4 li water
abt. 4 kg Terrana (balance) (4)
66.4 kg

Mixed 20 minutes

3). Hydrofluoric acid, techn. grade; I.G.Farbenindustrie, Leverkusen,
70 - 75%
HF, determined: 72.6%
D^{20} about 1.13
shipment of June 19, 1940

4). Iron hydroxide, techn grade, powdered; Merck
Catal. 3855
Iron content found 59.4%

5). Chromic anhydride techn grade, 99%, crystallized, Merck
CrO_3, by analysis 98.4%
Cr, " " 51.2%
Used in 40% solution.

6). Ammonium sulfomolybdate, 98-99%; Riedel & De Haen,
Mo content, from analysis 30.4%
used as 20% solution in ammonia, sp.gr. 0.910

7). Ammonia water, technically pure, 0.910
Bros Overlach, M.-Gladbach
NH_3 contents, from table. 25%

Compounding: 60 kg dry batch

Filling: 90 kg A.D.V (dry 36.0 kg).
Added: 2 kg $Fe(OH)_3$ (" 2.0 ")

Mixed 5 minutes

Added:
4.1 kg hydrofluoric acid
1 kg water
5 - 6 kg Terrana (dry 6 kg)

Mixed 30 minutes

Added:
6 kg chromic acid solution (2.4 kg solid)
2 liters water
abt. 15 kg terrana (dry 15 kg)

Mixed 10 minutes

Added next:
6 kg ammonia water
3 liters water

Mixed 10 minutes

Added next:
2 kg ammonium sulfomolybdate in solution in (2)
9 kg ammonia water
4 li water
abt. 4 kg Terrana (balance) (4)

65.4 kg

Mixed 20 minutes

Loading and emptying 18 mins
Total time per charge 1.5 hours.

Explanations:

1) Fe: 60 kg, 2% of that = 1.2 kg
$Fe(OH)_3$ (59.4%) = 2.02 kg
around 2 kg.

2) HF: 60 kg to 100 kg - 5 kg = 3 kg HF
Hydrofluoric acid 72.6% = 4.13 kg; around 4.1 kg

3) CrO_3: 60 kg of this amount abt. 2% Cr = 1.2 kg Cr
chromic acid = 51.2% Cr = 2.35 kg CrO_3
used in the form of 40% solution = 5.87 kg solution
around 6 kg.

4) Mo: 60 kg, 1% of this = 0.6 kg Mo
Sulfomolybdate 30.4% Mo = 1.97 kg. Around 2 kg.

5) NH_3 enough ammonia water must be added that the HF and CrO_3 are neutralized before the addition of the sulfosalt, with a slight excess of NH_3 being present.

72.6%
a) 1 kg HF/ requires 2.6 kg NH_3 (0.910)
4.1 kg HF 10.7 kg " "

b) 1 kg CrO_3 solution (40%) require 0.4 kg NH_3
6 " " " " 2.4 " "

Total 13.1 kg NH_3

The A.D.V. paste and terrana are also acid, and in order to obtain an excess,

6 + 9 kg = 15 kg were used.

Storing: The first 2 - 3 tonnes were stored 2 - 4 days before pressing.
Storage subsequently abt. 24 hours.

Pelleting: 12 mm rounded cylinders
10 mm rounded cylinders.

Drying: 5 days, at about 50 - 70°.

Activation: In furnaces: In boats, 300 - 600 lt vol.
gas H_2 stream
temperature 250° C, 17.6 mv.
time: 10 - 11 hrs to reach temperature
4 hours at temperature
8 hours cooling

Storage: In 250 - 250

Application: Delivered 8/5 to stall 54 A
Loaded with K 349 for the period of test
Start: 8/13/40: 4,520 kg = 6.88 m^3

Temperature log of activation: (v. original)

Start activation 7 o'clock
Temperature - 20° C
11 hours later, at 18 o'clock, the activation temperature 17.6 mv = 350° C was reached. Kept at this temperature till 22 o'clock. After that slowly cooled for 8 hours, till 6 o'clock.

MODIFIED K - 346

1) Beginning with July 1st, after mixing about 1.5 to. the mix was made thicker, by using [illegible] kg of water, instead of 10 kg.

2) The amount of water fluctuates depending on the outside temperature between 2 and 4 liters.
Mix stored before pressing for a few hours only.

INDUSTRIAL TESTING OF CATALYST

In 5 kg converter: G 22 in stall II
July 11 - August 6:
With make-up gas and circulation gas
With tar middle oil and coal middle oil (Scholven)

FACTORS FOR COMPUTATIONS

1) Capacity of stall 54 A is 10.9 m^3
With a filling weight of 0.66 - 0.68, this represents a charge of 7260 kg.

349

Preliminary tests:

In 5 kg converters: G 23 Stall I with K 349

It has been found that K 349 was just as good as K 346. It contains only half as much HF, which gave it an advantage over K 346 (lessened danger of burns and corrosion.)

TIME OF PREPARATION: July 24 - August 19, 1940

TOTAL PRODUCTION: 5,140 kg.

COMPOSITION: 60% A.D.5 paste
40% Terrana
2.5 g HF / 100 g carrier
- - - -
2% Fe as ferric hydroxide
2% Cr as CrO_3
1% Mo as sulfosalt.

RAW MATERIALS: as in K 346.

COMPOUNDING: like K-346, except for
2 kg hydrofluoric acid (instead of 4.1 kg)
2 kg ammonia (instead of 6)

STORAGE: like K 346

PELLETING: 10 mm rounded cylinders

DRYING: 50 days at 60 - 70°

ACTIVATION: Like K-346

USES:

CHANGES: The explosion in stall 54 on 8/17/40 has led us to suspect corrosion (by fluorine), and the temperature of activation was raised to 400° a 20.0 atm. (8/21/40)

CHANGES IN K 346: H_2O varies with the outside temperature.

INDUSTRIAL TESTING OF CATALYSTS: In the 5 kg converter: G 23 in Stall I, July 11 - September 5, 1940, with make-up gas and circulation gas; on pitch and coal middle oil.

K 362

PRELIMINARY TESTS.

5 kg converter: 1) G 18 with K 320 in stall I, 5/8/40 - 6/10/40
2) G 24 with K 362 in stall II, 8/15/40 - 8/18/40

In comparison with K 346 and K 349, K 320 has produced more constituents below 100°. Tests with G 24 were intended to prove if increasing the proportion of A.D.5 paste would produce this effect. This catalyst had been prepared at an earlier date because of terrana shortage.

TIME OF PREPARATION: August 19 - 21

TOTAL PRODUCTION: 750 kg.

COMPOSITION: Like K 346 and K 349, except for 80% A.D.5 paste
20% terrana

RAW MATERIALS: Same as K 246/249

ADDITION OF COMPONENTS: Same as K 349, only without additional ammonia.

STORAGE: Same as K 349

PELLETIZING: 10 mm rounded cylinders

DRYING: 5 days at 60 - 70°

ACTIVATION: Like K 346

STORAGE: In 250 - 260 li vessels

USES: 2,201.0 kg turned over on 7/17/40 to stall 17

K 368

PRELIMINARY TEST: in 5 kg converter: G 24 with K-362, stall II, 8/15-8/18-40

K 368 was only prepared because of the absence of terrana

TIME OF PREPARATION: August 18 - Aug. 25, 1940

TOTAL PRODUCTION: 1,619 kg.

COMPOSITION:
A.D.5 paste
2% Fe from $Fe(OH)_3$
2% Cr from CrO_3
1% Mo from $(NH_4)_2MoS_4$
2.5 g HF for 100 g. carrier

RAW MATERIALS: Same as for K 346, 349, 362

ADDITION OF COMPONENTS: Same as K 349, 362

STORAGE: Same as 349, 362.

PELLETIZING: 10 mm rounded cylinders

DRYING: 5 days at 60 - 70°

ACTIVATION:
Furnace: in baskets, cap. 500 - 600 li.
gas Stream of H_2
Temperature: 400° = 20.0 mv.
Time: Coming up to temperature -- 10 hrs
Kept at temperature -- 4 hrs
Cooling -- 6 hrs.

STORAGE: In 250 - 260 li containers

USES:

PRELIMINARY TESTS:

1) G.27 with K 381 Stall I 9/26 - 10/12, 1940	60% A.D.5 paste 40% terrana 2% Fe from $Fe(OH)_3$ 2% Cr from CrO_3 0.25% Mo from $(NH_4)_2MoS_4$ 2.5 g HF/100 g. carrier
~~2) G.28 with K 382~~ Stall II 9/26 - 10/12, 1940	~~60% A.D.5 paste~~ 40% terrana 4% Cr from CrO_3 2.5 g HF/100 g carrier
3) G.29 with K 391 Stall II 10/17 - 10/28, 1940	60% A.D.5 paste 40% Terrana 2% Fe from $Fe(OH)_3$ 2% Cr from CrO_3 0.4% Mo from $(NH_4)_2MoS_4$ 2.5 g HF/100 g. carrier
4) G.31 with K 391 Stall II 10/25 - 11/6, 1940	60% A.D.5 paste 40% Terrana 2% Fe from $Fe(OH)_3$ 2% Cr from CrO_3 0.4% Mo from $(NH_4)_2MoS_4$ 2.5 g HF/100 g. carrier
5) G.32 with K 406 Stall I 11/7 - 11/19, 1940	60% A.D.5 paste 40% Terrana 2% Cr from CrO_3 5% Pb from $Pb(CH_3COO)_2 \cdot 3\ H_2O$ 0.4% Mo from $(NH_4)_2MoS_4$ 7.5 HF / 100 g. carrier
6) G.33 with K 413 Stall II 11/9 - 11/17, 1940	60% A.D.5 paste 40% Terrana 2% Cr from CrO_3 5% Zn from ZnO 0.4% Mo from $(NH_4)_2MoS_4$ 7.5 g HF / 100 g carrier
7) G.34 with K 422 Stall II 11/20 - 11/27, 1940	60% A.D.5 paste 40% Terrana 2% Cr from CrO_3 4.5% AlF_3 0.4% Mo from $(NH_4)_2MoS_4$ 7.5 g. HF / 100 g carrier
8) G.35 with K 421 Stall I 11/22 - 12/15, 1940	60% A.D.5 paste 40% Terrana 2% Cr from CrO_3 2% Pb from $Pb(CH_3COO)_2$ 0.4% Mo from $(NH_4)_2MoS_4$ 7.5 g HF/100 g. carrier

9) G.36 with K 429	60% A.D.5 paste 40% Terrana
Stall II	2% Cr from CrO_3 1% Pb from $Pb(CH_3COO)_2$
11/30 - 12/15, 1940	0.4 Mo from $(NH_4)_2MoS_4$ 7.5 g HF / 100 g carrier

TIME OF PREPARATION: 11/26/40 - 4/30/41

TOTAL PRODUCTION: 21,766 kg

COMPOSITION:
60% A.D.5 paste
40% Terrana
2% Cr from CrO_3
1% Pb from $Pb(CH_3COO)_2$
0.4% Mo from $Me(NH_4)_2MoS_4$
7.5 g HF / 100 g carrier

RAW MATERIALS:

1)	A.D.5 paste:	Ver. Bleicherde Fabriken, München shipment of 9/7/1940 H_2O content = 60%
2)	Terrana, extra	Do, shipment 8/16/1940
3)	Hydrofluoric acid, tech.:	I.G.Farbenindustrie, Leverkusen, 70 - 75% HF content, by titration = 72.6% shipment of 8/17/40; sp.gr. abt 1.13
4)	Chromic anhydride, techn.:	Merck, Darmstadt. 99% cryst. CrO_3 content, by analysis, = 98.4% Cr content " " = 51.2% Used in 40 - 45% solution
5)	Lead acetate	Merck, Darmstadt Shipment of 12/2/40; Pb content, theoretical 54.6% used in 46% solution
6)	Ammonium sulfomolybdate:	98 - 99% from Riedel E. de Haen Mo content, by analysis, 30.4% Used as 8.9 solution in 0.910 NH_3
7)	Aqua ammonia:	Technically pure; sp.gr. 0.910 Overlack Bros. M.-Gladback NH_3 content, from table, 25%

PREPARATION: 90 kg A.D.5 paste (= 36.0 kg dry material)

added to it: 6.2 kg HF
0.25 kg water
about 7.0 kg terrana (= 7.0 kg dry)

Kneaded for 10 minutes

Added to it: 5.3 kg H_2CrO_4 solution (= 2.4 kg dry)
0.25 kg H_2O
12.0 kg terrana (= 12.0 kg dry)

Kneaded for 10 minutes

Added to it: 1.1 kg lead acetate (1.1 kg dry)

Kneaded for 10 minutes

Added to it: 11.8 kg aqua ammonia

Kneaded for 10 minutes

Added to it: 0.8 kg ammonium sulfomolybdate, dissolved in (0.2 dry)
8.2 kg aqua ammonia
4.0 kg terrana (4.0 dry)

Kneaded for 20 minutes

total 63.3 kg dry material

Filling and emptying 15 minutes

TOTAL TIME PER BATCH 2 hours

STORING: the catalyst was used immediately

PELLETIZING: 10 cm rounded cylinders

DRYING: the first 10 m^3 were dried for 4 days at 50-70°
the rest for 5 days at 50-70°

ACTIVATION: In furnace: in boats, 500 - 550 li cap.
Gas H_2 stream, 120 - 140 m
Temper.: 350° = 17.6 mv
Time: 10 hours to reach temperature
4 hours at temperature
8 hours cooling

STORAGE: in 250 - 270 li vessels

USE: Stall 54 A was charged 12/18 - 12/22/40 with the following amount: 6,633.5 kg = 19.7 m^3 K 429. 10 mm rounded cylinders.

In addition, the following amounts of K 429 were delivered to Stall 54:

1/19/41	4,458 kg	7,200 li
3/31/41	3,876 "	6,250 "
6/11/41	1,900 "	3,070 "
6/27/41	1,768 "	2,850 "

FIGURES FOR ACCOUNTING:

Determination of filling weight:

in container 44:

container filled to upper edge with water	269.0 li
" " " " " " K 429	166.7 kg

Filling weight 0.62 to/m³

INDUSTRIAL TESTING OF THE CATALYST:

in 5 li converter, test G 36, Stall II, 11/30 - 12/15/40

Circulation gas used, with tar middle oil and tetraline

in 5.0 li converter, test G.37, stall I, 12/25/40 - 1/20/41
with circulation gas and tar middle oil

TEMPERATURE LOG OF ACTIVATION:

Start of activation 8 o'clock
temperature + 20°

After 10 hours, at 18 o'clock the activation temperature of 17.6 mv = 370° was reached. Kept at that temperature until 22 o'clock. Cooled slowly for 8 hours until 7 o'clock (sic)

K 446

BASIS OF THE PREPARATION OF CATALYST K 446

The A.D. 5 paste, delivered 12/27/40, has lost much water through freezing. This made the paste too thick. In order not to add too much water, the terrana contents were reduced by 10%.

PRELIMINARY TESTS. The same tests as with K 429

TIME OF PREPARATION: 2/1/41 - 5/30/41.

TOTAL PRODUCTION: 10,744 kg

COMPOSITION:
- 70 parts A.D. 5 paste
- 30 parts terrana — 7.5 g HF / 100 g carrier
- 2 " Cr from CrO_3
- 1 part Pb from $Pb(CH_3COO)_2 \cdot 3H_2O$
- 0.4 part Mo from $(NH_4)_2MoS_4$

Raw material, compounding, storing, pelletizing, drying, activation, storage and use as with K 429

DELIVERIES:
3/31/41: 6,673 kg = 10,760 li
6/12/41: 2,496 kg = 4,020 li

K 413

COMPOSITION:
60 parts A.D. 5 paste; to 100 g carrier 7.5 g HF
40 " terrana
2 " Cr from CrO_3
5 " Zn from ZnO
0.4 (5) parts Mo from $(NH_4)_2MoS_4$

Total S, by analysis - 0.63%
0.59%
Mo, by analysis 0.58%

TIME OF PREPARATION: 7/1/41 - 8/14/41 17 mm hollow pieces
11/25/41 - 1/5/42 10 mm rounded cylinders

TOTAL PRODUCTION: 7,945.8 kg = 17.65 m^3 17 mm hollow pieces
10,926.5 kg = 17.90 m^3 10 mm rounded cylinders

RAW MATERIALS:

1) A.D.5 paste Süd-Chemie, München, shipment 4/2/41; 60% H_2O

2) Terrana, Extra Süd-Chemie, München, shipment 2/19/41

3) hydrofluoric acid, techn. grade.
I.G.Farbenindustrie, Leverkusen, 70 - 75%
HF content by titration: 72.6% sp.gr. 1.13
Dr. Reininghaus, Essen ~~66 - 70%~~
HF content by titration: 60.2%; sp.gr. 1.13

4) Chromic anydride, techn. grade.
Merck, Darmstadt, 99% crystallized
CrO_3 content, by analysis 98.4%
Cr content, by analysis 51.2%
Used in 45% solution

5) Sinc Oxide, techn. grade, from stock (Building 54)
Zn content - 80.4% (theoretical)

6) Ammonium sulfomolybdate, 98 - 99%, Riedel E.de Haen
Mo content, by analysis 30.4%
used in 10% solution in aqua ammonia, sp.gr. 0,910

7) Aqua ammonia, technically pure, sp.gr. 0.910
from Overlack Bros. M.-Gladbach
NH_3 content, from tables, 25%

COMPOUNDING: 64 kg dry charge

Filling 90.0 kg A.D.5 paste = 36.0 kg dry

Addition of 6.2 kg hydrofluoric acid water, depending upon the consistency of the paste
7.0 kg terrana 7.0 kg dry

Kneaded for 30 minutes

addition of 5.6 kg H_2CrO_4 soln 2.5 kg. dry
12.0 kg terrana 12.0 dry

Kneaded 10 minutes

addition of 4.0 kg ZnO 4.0 kg dry

Kneaded 10 minutes

addition of 11.0 kg aqua ammonia

Kneaded 10 minutes

Addition of 1.05 kg $(NH_4)_2MoS_4$ in 9.0 kg aqua ammonia 1.05 kg dry
5.0 kg terrana 5.0 kg dry

kneaded 30 minutes 67.55 kg

Filling and emptying 15 mins;
Total time per charge 2 hours

STORING: The catalyst mass was immediately pelleted.

PELLETING: 17 mm hollow pieces - 10 mm rounded cylinders

DRYING: Dried in 3 days at 60 - 70° (hollow pieces)
" " 4 " " 60 - 70° (cylinders)

ACTIVATION: Furnace: in boats, 500 - 550 l capacity
Gas: stream of N_2 120 - 140 mm.
Temper. 400° - 20.0 mv.
Time: to temperature in 8 hours
at temperature for 4 hours
cooling 10 hours

STORAGE: In 250 li iron containers (Mauser)
9,835.6 kg = 16.1 m^3 of rounded cylinders
delivered to stall 54a from 1/7 to 1/13/42
7,945.8 kg hollow pieces delivered on 5/15/42 to
the hydrogenation division for use in Building 91.

DETERMINATION OF FILLING WEIGHT OF HOLLOW PIECES:
In container 52 with cover:
filled to top with water 262.5 kg
" " " " K 413 149.5 kg
Filling weight 0.45 te/m^3

DETERMINATION OF FILLING WEIGHT OF 10MM ROUNDED CYLINDERS:

In container 58, with cover:
Filled to top with water 266.8 kg
" " " " K 413 162.5 kg
Filling weight 0.61 te/m^3

The determination run in duplicate.

TEMPERATURE LOG DURING ACTIVATION:

Start of activation 8 o'clock
Temperature + 20°

8 hours later, at 16 o'clock, the temperature of activation, 20.0 mv = 400° C was reached. This temperature kept till 20 o'clock. Cooled slowly for 10 hours until 6 o'clock.

INDUSTRIAL TESTING OF CATALYSTS.

K 534

PRELIMINARY EXPERIMENTS:

COMPOSITION: 60 parts by weight A.D.5 paste 7.5 g HF/100 g dry paste
40 " " " terrana

5 g ZnO to 100 g carrier
2 g Cr from CrO_3 " " " "
5 g flowers of sulfur " " " "
0.7 g Mo from $(NH_4)_2MoS_4$ " " " "

S content, by analysis 2.25%
Mo " " " 0.54%

TIME OF PREPARATION: 3/9/42 - 6/30/42
1/12/42 - 1/9/43

TOTAL PRODUCED: 22,031.0 kg = 33.4 m^3 10 mm rounded cylinders.
9,310.7 " 14.1 " " " " "

RAW MATERIALS:

1) A.D.5 paste, from Südchemie, München.
Shipments of 3/17 and 5/13/42; 60% water

2) Terrana, extra, from Sud-Chemie, München; shipment of 3/28/42

3) Hydrofluoric acid, techn. grade
From Dr. Reininghaus, Essen, 70 - 75%
By titration HF - 72.6% sp. gr. 1.13
Shipments of 12/5/41, 12/13/41, 1/17/42, 1/29/42,
3/4/42 and 5/6/42

4) Chromic anhydride, technical grade
From Merck, Darmstadt, 99.0%, crystallized.

CrO_3 content, by analysis	98.4%
Cr content, by analysis	51.8%

Used in 45.0 - 50.0 % solution
From shipments of 12/29/41, 4/20/42 5/15/42

5) Zinc oxide, technical
From Zinkindustrie, Hamborn, shipment of 3/27/42

6) Sulfur, 95 - 100°
From Dr. Reininghaus, Essen, Shipments of 2/13, 3/18 3/26 and 4/22/42.

7) Ammonium sulfomolybdate, 98 - 99%. From Riedel de Haen. The Mo content is always determined after the receipt of a shipment, and operations run on the strength of the analysis. The value varied between 30.0% and the theoretical value (36.9%). When the water was too high, (>2%), it was deducted. Used as 10% solution in aqua ammonia.

8) Aqua ammonia, techn. grade, 0.910
From Overlack Bros., M.-Gladbach
NH_3 contents from tables = 25.%
Shipments of 2/17, 4/12 and 6/5/42 (From Reininghaus)

COMPOUNDING 65.0 kg dry charge.

Filling	97.5 kg A.D. 5 paste	= 36.00 kg dry
~~addition of~~	~~4.1 kg hydrochloric acid~~	
	water depending on the consistency of the paste	
	8.0 kg terrana	8.0
	Kneaded 30 minutes	
addition of	3.25 kg ZnO	3.25
	5.0 " H_2CrO_4 soln	2.50
	8.0 " terrana	8.00
	Kneaded 10 minutes	
addition of	7.0 kg NH_4OH	
	Kneaded 10 minutes	
addition of	3.25 kg flowers of sulfur	3.25
	Kneaded 10 minutes	
addition of	1,320 g $(NH_4)_2MoS_4$ in 9.3 kg NH_4OH	1.32
	10.0 kg terrana	10.00
		72.32 kg. dry weight

Kneaded 20 minutes

Filling and emptying 15 mins
Total time per charge 1-3/4 hours

STORING: The catalyst mass was used immediately

PELLETING: 10 cm rounded cylinders.

DRYING: 3 - 4 days at 60 - 70°.

ACTIVATION: in furnace: boats, 500 - 600 li capacity
gas: stream of N_2
Temper.: 350° = 17.6 mv
Time: To temperature 8 hrs
at temperature 4 hrs
cooling 10 hrs

STORAGE: In bins and 250 li Mauser containers.

USE: 7,806.2 kg = 11.82 m^3 delivered to stall 54a on Oct. 21

TEMPERATURE LOG OF ACTIVATION:
Start 9 o'clock; temp. + 20°
17 o'clock, activation temper. reached 350° = 17.6 mv
to 21 o'clock, kept at temperature; cooled to 6 o'clock

INDUSTRIAL TESTING OF CATALYST:
In 5.5 li converter Stall II
G.63, 3/26 - 4/1/42
G.64, 4/6 - 4/21/42
G.65, 4/24 - 5/3/42
G.66, 5/6 - 5/16/42
G.67, 5/21 - 6/24/42

K 535

The method of preparation of K 535 is the same as of K 534, except that the S was increased from 5 to 10 g / 100 g carrier.

COMPOSITION: 60 parts by weight of A.D.5 paste, 7.5 g HF/100 g dry paste
40 " " " terrana extra

5 g ZnO Per 100 g carrier
2 g Cr as CrO_3 " " " "
10 g S flowers " " " "
0.7 g Mo as $(NH_4)_2MoS_4$ " " " "

Mo by analysis 0.55%
S " " 4.10%