INFORMATION REPORT INFORMATION REPORT

CENTRAL INTELLIGENCE AGENCY

[redacted]

S-E-C-R-E-T 50X1-HUM

COUNTRY	Poland	REPORT	[redacted]
SUBJECT	1. [redacted] the Use of Liquid Gas at Blachownia and Coke-Oven Gas at the Kedzierzyn Nitrogen Plant	DATE DISTR.	24 JUL 1964
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[redacted] 50X1-HUM

(1) The [redacted] translation, of a technical report drawn up at the Institute for Heavy Chemical Synthesis in Blachownia which contains (a) resolutions adopted at a conference called for the purpose of analyzing the composition of liquid gases and (2) a compilation of pertinent data regarding their use.

(2) [redacted] translation, of a document containing technical data on coke-oven gas delivered to the Kedzierzyn Nitrogen Plant (Zaklady Przemyslu Azotowego "Kedzierzyn"). 50X1-HUM

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OSI	:	Retention of 1 copy of translation
ORR	:	Retention of 1 copy of translation
DIA	:	Retention of 1 copy of translation

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STATE	DIA	ARMY	NAVY	AIR	NSA	XX		
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EXPEDITE

Technical Data of Coke-Oven Gas delivered to Z.P.A. KĘDZIERZYN

The gas is supplied by: Z.K. ZDZIESZOWICE and Z.G.O.Z.

1. According to current analyses made by ZGOZ, ICSCh KĘDZIERZYN, and the Laboratory and Research Institute of ZPA KĘDZIERZYN, composition of the gas is as follows:

	Component	Boundary Values	Most frequently occurring value
1.	H_2	52 - 59%	55%
2.	N_2	3 - 6%	4%
3.	O_2	0,4 - 1,6%	0,7%
4.	CO	6 - 12%	9%
5.	CH_4	20 - 28%	25%
6.	C_2H_4	1,4 - 2,5%	2,1%
7.	C_2H_6	0,4 - 0,7%	0,5%
8.	C_3H_6	0,2 - 0,6%	0,4%
9.	C_2H_2	0,04 - 0,14%	0,09%
10.	CO_2	2,8 - 4,2%	3,2%
11.	H_2S	0 - 3g/100Nm^3	1,5g/100Nm^3
12.	HCN	5 - 7g/100Nm^3	6g/100Nm^3
13.	Sorganic	7 - 40g/100Nm^3	8g/100Nm^3
14.	naphthalene	9 - 15g/100Nm^3	10g/100Nm^3
15.	benzol	1,5 - 15g/Nm^3	4g/Nm^3
16.	NO x)	$0,1 \times 10^{-5} - 4 \times 10^{-4}$ %	

x) by the "Grande Paroisse" method

Remark: Values in column (4) are not computed averages, but represent the most frequently occurring composition of the gas.

2. The composition of the gas listed above shows the content of various impurities to be comparatively high if compared with gas analyses from other Polish and foreign cokeries. Particularly disadvantageous are the analyses of CO_2, C_2H_2, NO, and benzol. Here are some examples:

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Czechoslovakia, cokery "Sverma" at Moravska Ostrava:

content of	CO_2	max.	2,5%
	C_2H_2	max.	0,05%
	NO	max.	3×10^{-5} %

Cokery "Knurów": content of benzol aver. 1,6g/Nm^3.

German Federal Republic Dalgaz: content CO_2 aver. 2,9%.

In addition our representatives have visited the GFR and France in 1958 and have examined the composition of gas from various cokeries: they have not met with such high contents of C_2H_2, CO_2, and NO, and values cited came to them as a surprise.

We believe it possible to lower the amount of impurities in the gas through appropriate management of the technological process, by insuring the leak-proofing of chambers (CO_2,NO), by correct operation of the benzol plant (C_6H_6), through removal of NO prior to de-sulphurization. In addition, impurity content and gas composition are greatly influenced by selection of appropriate coal (lowering of H_2S and organic sulphur content, increase of hydro-carbons, particularly of ethylene).

3. Cokery-gas composition and impurities contents required by KEDZIERZYN:

	Component	Boundary values
1.	H_2	52 - 58%
2.	N_2	3 - 6%
3.	O_2	0,7 - 0,9%
4.	CO	6 - 10%
5.	CH_4	22 - 30%
6.	C_2H_4	2 - 6,5%
7.	C_2H_6	max. 1,5%
8.	C_3H_6	max. 1,5%
9.	C_2H_2	max. 0,08%
10.	CO_2	max. 3,3%
11.	H_2S	max. 2g/100 Nm^3
12.	HCN	max. 7g/100Nm^3
13.	S organic	max. 10g/100Nm^3
14.	naphthalene	20 g/100 Nm^3 (winter) 30 g/100 Nm^3 (summer)
15.	benzol	2 g/Nm^3 (winter) 2,5 g/Nm^3 (summer)
16.	NO x)	max. 0,5g/Nm^3, i.e., $3,7 \times 10^{-5}$ %

x) by the "Grande Paroisse" method.

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Gas pressure at ZPA KĘDZIERZYN should be 3 ata, in view of working conditions of the gas compressors purchased by ZPA.

We propose to base calculation with the supplier on composition of the gas and not on its caloric value. With this method of accounting we would be paying for components which are important for us, i.e., for hydrogen, methane, and ethylene; at the same time, the cost of the gas would decrease whenever impurity contents would rise above the guaranteed values.

(Planned increase of production capacity at Z.K. ZDZIESZOWICE)

1.3.4.3. Yearly production at ZDZIESZOWICE resulting from increase

1.3.4.3.1. Yearly basic production at ZDZIESZOWICE after increase.

	Product	Unit	blocks 1 - 2	under constr. blocks 1 - 4	Plan for 1966 blocks 1 - 6
1.	coke total (7% H_2O)	tons	718320	1476148	2233976
2.	coke over 40 mm	"	617580	1238629	1859678
3.	coke, lump over 60 mm	"	-	469483	938966
4.	coke, "nut I" (40-60 mm)	"	-	151566	303132
5.	coke, "nut II" (20-40 mm)	"	64824	133215	201604
6.	coke, pea size (10-20 mm)	"	21900	45005	68110
7.	coke, tiny (0-10 mm)	"	42924	88209	133494
8.	coke, tiny I (6-10 mm)	"	-	26802	53604
9.	coke, tiny II (0-6 mm)	"	-	18483	36966
10.	physical gas (ca 4300 kcal/ /Nm^3/10^3 Nm^3	"	285576	596100	906624
11.	tar (5% H_2O)	"	28908	62178	95448
12.	ammonium sulphide (1,5% H_2O)	"	9636	18878	28120
13.	pyridine bases 60%	"	87,6	180	272,4
14.	raw benzol (95% at 180° C)	"	9706	21073 / 21678	32440 / 33550
15.	sodium phenolate (ca 30%)	"	1226	2520	3814
16.	sulphuric acid 100%	"	-	4621 6561 / 5490 7837	9242 13122 / 10980 15674
17.	potassium ferrocyanide 99%	"		48,6/69,5	97,2/139

1.3.4.3.2. Production of ZDZIESZOWICE auxiliary divisions before and after capacity increase.

	Product	Unit	blocks 1 - 2	blocks 1 - 4	blocks 1 - 6
1.	steam	t/h	40/50	20/100	120/130
2.	electrical energy	MWh/h	2,4	5,6	7,8
3.	quencher car gas ($Wd=1180$ kcal/Nm^3/$10^6 Nm^3$/year)		-	504	1008

1.3.9. Amount used per year and supply sources of raw material and first-order auxiliary materials in tons.

1.3.9.1. Yearly consumption of raw material.

	Raw material	blocks 1 - 2	blocks 1 - 4	blocks 1 - 6	use factor
1.	Dry coal	876000	1800180	2724360	1220 kg/T.K.M.
2.	Wet coal (8% H_2O)	952174	1956717	2961260	1326 "
3.	Coal type 36/38	171391	352209	533027	238 "
4.	Coal type 35	95217	195671	296126	133 "
5.	Coal type 34	399914	821822	1243729	557 "
6.	Coal type 33	285652	587015	888378	398 "
7.	Energy-producing coal for power/heatingplants	46000	120000	156000	-

The raw material is domestic coking coal, with a possible addition of "type 35" coal imported from the USSR.

Remark: the same use factors for individual types of coal were used in all stages of planned capacity increase.

1.3.9.2. Yearly need for first-order auxiliary materials:

	Auxiliary Material	blocks 1 - 2	blocks 1 - 4	blocks 1 - 6	use factor
1.	Sulphuric Acid 78% for am.sulph. prod.	9389	18395	27400	974,4 kg/t am.sulph.
2.	Calcium Oxide (80% CaO) for separation of combined amm.hydroxide	578	1133	1687	0,060 t/t amm.sulph.
3.	Absorption Oil	1165	2429 / 1942	3893 / 2717	0,120 / 0,070 t/t raw benzol.

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COAL: total production is ca 106 million tons/year.
An increase is planned of ca 10%.

At present, coal seams in the RYBNIK BASIN are producing ca 300 million m^3 of natural gas, containing ca 70% methane (the rest is air). For this natural gas, a pipeline is being constructed to OSWIĘCIM and is now almost completed. At present possibilities are being discussed regarding the use of the gas in chemistry (besides heating of boilers).

COKE and SEMICOKE:

At ZDZIESZOWICE two more coke-furnace blocks are under construction and almost finished. Thus this plant now has four coke-furnace blocks with a yearly capacity of 1,476.148 tons of coke (7% water contents). The plan for 1966 provides for two additional blocks. After this enlargement production of coke will come to 2,233.976 tons per year, which is equivalent to 2,724.360 tons of dry coal. It is of interest that:

(1) part of the demand for coking coal will probably be made up by imported Soviet coal;
(2) pyridine bases are being obtained:
blocks I and II are providing 87,6 tons/year -
blocks I to VI will provide 272,4 tons/year.
(3) sodium phenolate is obtained (by water de-phenolization) from blocks I and II: 1.226 tons/year;
blocks I to VI will produce 3.814 tons/year.
(4) production of sulphuric acid 100% concentrated in blocks I to IV will rise from 4.621 to 7.847 tons/year;
blocks I to VI will produce up to 15.674 tons/year.
(5) ferrous potassium cyanide 99% concentrated:

blocks I to IV	48,6	to	69,5	tons/year -
blocks I to VI	97,2	to	139	tons/year.

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At OSWIĘCIM there are four LURGI-made low-temperature coke furnaces (for semicoke production) in operation. Two more are in the construction stage, and four more are planned.

Estimated production for ten units is 3.500 to 5.000 tons/year, depending on the quality of the coal. At present the major part of this semicoke is used in continuous-type furnaces (tunnel kilns) at BLACHOWNIA (BLECHHAMMER) to produce blast-furnace coke in the form of pillow-shaped briquettes by a process developed at the INSTYTUT WĘGLA (COAL INSTITUTE) in BISKUPICE. For this reason, the low-temperature coke now produced at OSWIĘCIM contains only 4% volatile parts. The semicoke is transported to BLACHOWNIA and crushed there.

Allegedly, the quality of coke produced in the tunnel kilns is not yet satisfactory for use in blast-furnaces. Nevertheless, existing plans provide for an increase of the number of tunnel kilns to reach a yearly production of 600.000 tons. This is an indication of the existing shortage of coking coal, as well as of the planned development of the steel producing industry.

It is planned (in cooperation with the LURGI Company) to manufacture low-temperature gas in the above mentioned low-temperature coke furnaces in undiluted form, and to heat the furnaces with other gases if possible.

For the city of WARSAW a gas conversion plant is being planned instead of a new coal degasification plant.

NATURAL GAS:

domestic production	800 million m^3/year
suppl. import from Soviet Union	1.000 million m^3/year
import from Soviet Union after 1966	2.000 million m^3/year

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INDUSTRIAL USES OF CRUDE OIL:

PŁOCK

Development Stage I 6 million tons/year
(construction by ENI Company and "Snam PROGETTI)

Development Stage II 12 million tons/year.

The oil used is Soviet crude oil (so called "ropa romaszkinska").

Operation of the pipeline will start this year (1963) on the day commemorating the October Revolution.

Of the PŁOCK production, 200.000 tons of gasoline and 200.000 tons of liquid gas will be cracked into ethylene. 200.000 tons of this ethylene will be processed at the BLACHOWNIA plant.

A pipeline is planned from the CZECHOWICE refinery to the OŚWIĘCIM plant for transporting of gasoline and liquid gas which is also to be used for ethylene production. (Allegedly, ethylene is manufactured at present only from coke-oven gas).

PETRO-CHEMISTRY and SYNTHESIS:

PŁOCK:

Besides now existing centers of organic chemistry, i.e., of synthesis and petro-chemistry, another such plant appears to be shaping up in PŁOCK (it was not possible to establish its connection with the refinery, nor its special objectives). It seems that there exists already at PŁOCK a synthetic production of phenole based on the VON HOCK process (either from propylene and benzol coal naphtha through oxydation of the resulting cumol, or by oxydation of cumol which is derived from cokery benzol).

It appears that there are plans for the manufacture at PŁOCK of tetra-propylene (for production of detergents) and, in addition, to build an installation for production of low-pressure polyethylene.

OSWIĘCIM:

In addition of the already existing production of 20.000 tons/year of acet-aldehyde, a new installation is planned for about the same amount of aldehyde derived from ethylene. Furthermore, a plant for about 35.000 tons/year of ethylene-benzol (for production of butadiene natrium (synthetic rubber) from styrol).

For the necessary ethylene production two installations are planned with an output of 15.000 tons/year each of ethylene obtained from cracking of gasoline or liquid gas, respectively. The above mentioned manufacture of synthetic rubber would constitute a supplement to the already existing production from acetylene and benzol.

According to Source, increase of acetylene production through construction of additional carbide furnaces is not possible for lack of space. At present three carbide furnaces are in operation, and a fourth one for 40.000 KW (cost: 16 million zł) is now being build, again by the Soviets. Thus, after completion of this unit, total carbide production at OSWIĘCIM will amount to 240.000 - 246.000 tons/year. The cost of electric power for carbide production is 0.40 zł/kwh.

At OSWIĘCIM, part of the acetylene is used for production of polyvinyl chloride (at present 25.000 tons/year).

It is planned, but not yet decided, to use propylene - which is obtained together with ethylene by cracking of gasoline and liquid gas - for the manufacture of glycerin, of oxo-alcohols (by the ROELEN process of "RUHRCHEMIE"), and of butanol (iso-butanol and chlorinated products). The same is considered for other planned ethylene-producing plants.

BLACHOWNIA is also to crack gasoline or liquid gas into ethylene. The amount considered is ca 200.000 tons/year, which will produce about 70.000 tons/year of ethylene. Conflicts, as well as discussions, are still going on regarding the process which is to be used

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(either cracking in externally-heated pipes in the presence of steam; or, through direct heating by a dust- or grain-shaped heat-transfer agent, f.ex., LURGI sand-cracker, or HOECHST process, or the new BASF process, or the KELLOG process.) Apparently one is inclined to use a process based on direct transfer of heat, allegedly because of the shortage in production of high-quality steel.

An important factor seems to be here the interest in the aromatic substances contained in the residue and, most of all, the possibility to crack heavy fractions. In contrast to the West, it is, for the time being, not yet possible nor desired to make use of fuel oil from refineries for direct production of energy, or in central heating plants, etc.

In regard to BLACHOWNIA there are plans to partially convert ethylene into high-pressure poly-ethylene. The necessary installation has already been ordered in England.

Allegedly, plans were also made for BLACHOWNIA to continue extension of the existing tar distillation facilities and tunnel kilns (see above). Apparently, production of briquette coke in the tunnel kiln, or in the two tunnel kilns, is ca 500 tons/day.

KĘDZIERZYN:

Main production at this plant is still synthesis of ammonia. At present the production quota is 800 tons/day. An increase is planned to 1.000 tons/day. Besides the existing production of gas for synthesis (and acetylene) from methane and coke-oven gas, respectively, in BASF-SACHSSE furnaces, there is apparently a fierce struggle going on regarding the practicability in future expansion plans, of cracking coke-oven gas at low temperatures for production of gas for synthesis. An order was placed with L'AIR LIQUIDE of France, for a 220 million m^3/year unit for low-temperature

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fractional distillation. At present, the majority seems to be against gas dissociation and for straight conversion of the total gas to gas for synthesis (similar as in the West). Aside from the problem of cost, evidently one does not know what to do regarding the methane fraction of the dissociated gas. At the moment it is being burned under the boilers.

For the actual NH_3-synthesis a MONTECATINI installation is under construction. In view of non-observance of delivery dates, one is apparently dissatisfied with the progress in delivery and construction, as well as quality of the material.

TARNOW:

A plant for manufacture of 40.000 tons/year of polyvinyl chloride is under construction. The manufacturing process is based on acetylene. An already existing installation is going to be modernized. For the future, the same problem is shaping up as for the plants OŚWIĘCIM, BLACHOWNIA, etc, namely the use of either acetylene or ethylene as raw material for this synthetic product (the problem of raw material and costs!).

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INSTITUTE FOR
HEAVY CHEMICAL SYNTHESIS
IN BLACHOWNIA/SILESIA

The following is an outline of a proposal which was compiled as a result of a conference called by the director of the Industrial Combine for Chemical Synthesis to analize the composition of liquid gases.

BLACHOWNIA/Silesia, 10 October 1963.

Present at the conference:

1. J. BERES, MA - Institute for Heavy Chemical Synthesis
2. M. MARQUARDT, MA eng. - "Projects for Chemical Synthesis"
3. St. ZUREK, MA eng. - Cokery Plant BLACHOWNIA
4. L. PINCZUK, MA eng. - Office for Industrial Projects
5. A.MIZGALSKA, MA eng. - Projects & Construction Office KĘDZIERZYN
6. M. JURDZIAK, MA eng. - Projects & Construction Office KĘDZIERZYN
7. St. ŁOSKOT, MA eng. - Authority for the PŁOCK Refinery
8. L.NOWAKOWSKI, MA eng. - Institute for Heavy Chemical Synthesis.

After an alalysis of the amounts and composition of liquid gases which will be produced at the PŁOCK refinery for the period 1964 - 1970, the following resolutions were accepted:

1/ Liquid gases offered by the PŁOCK refinery Authority during the period 1964 - 1970 with contents listed in the memo from the conference at Industrial Combine for Chemical Synthesis on 31 July 1963, are acceptable as raw material for cracking at the Cokery Plant in BLACHOWNIA.

2/ In order to insure productiveness of ethylene and propylene on a level corresponding to the expected one in the case of the cracking of gasoline, it is necessary to raise the temperature of the reaction to 780° C, which should not reflect to a major degree on the life span of the furnace.

The temperature of 800° C, although technologically possible, and insuring larger yields of ethylene, is not acceptable in view of

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difficulties involved in the installation of the distribution equipment which are caused by a considerable increase of methane and hydrogen content in gases after cracking.

3/ In order to insure correct working of the entire installation it was assumed that during the first period only one furnace will operate on liquid gases, the other on gasoline. After the extension of the installation, two furnaces will operate on liquid gases, and two on gasoline.

4/ At an operating temperature of 780° C, and with half of the cracking based on liquid gases (see par. 3), installation of the distribution will not require major changes.

5/ The committee is asking the Administration of Oil Industry (ZPN) and the Administration of Chemical Synthesis Industry to speedily sign a contract for deliveries of raw material for cracking to the Cokery Plant in BLACHOWNIA/Sil.

6/ The BLACHOWNIA Cokery Plant expects considerable difficulties in constructing the storing facilities for liquid gases on the prescribed date as well as increasing the storing facilities at the cracking installation. BLACHOWNIA is therefore asking the Administration of Chemical Synthesis Industry to make the necessary decisions regarding allocation of funds and designating who will do the construction.

7/ Attached to this report is a compilation of data pertinent to introduction of the new raw material.

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Calculation Summary

Calculations were made for the following three alternatives:

A – Cracking furnaces convert gasoline only

B – Half of the furnaces convert gasoline, the other liquid gases

C – Cracking furnaces convert liquid gases only.

Calculations are for two periods:

period I: 1965 – 1966

period II: 1967 – 1969.

1. Cracking at 800° C – period I – TABLE I:

		A	B	C
gasoline consumption	t/h	12,4	6,2	–
consumption of liquid gases	t/h	–	5,09	10,16
dry gas for distribution	Nm^3/h	10.638	10,028	9416
wet gas for distribution	Nm^3/h	8360	8760	9280
ethylene content in the gas	kg/h	2744	2744	2744
gas composition % weight/% volume				
H_2		0,81 / 12,06	1,0/13,8	1,4/15,8
CH_4		13,94 / 25,81	19,2/31,7	25,1/37,2
C_2H_2		1,39 / 1,60	0,8/ 0,9	0,1/ 0,1
C_2H_4		25,81 / 27,20	27,4/25,9	29,2/24,5
C_2H_6		6,60 / 6,51	7,5/ 6,7	8,6/ 6,7
C_3H_6		15,00 / 10,60	13,7/ 8,6	12,1/ 6,8
C_3H_8		1,37 / 0,93	2,3/ 1,4	3,3/ 1,8
C_4		12,52 / 6,75	10,5/ 5,2	8,1/ 3,6
C_5 + w		22,58 / 8,54	17,6/ 5,8	12,1/ 3,5
		100,00 100,00	100,00 100,00	100,00

2. Cracking at 780° C - period I - TABLE II:

		A	B	C
gasoline consumption	t/h	12,4	6,2	-
consumption of liquid gases	t/h	-	6,74	13,48
dry gas for distribution	Nm^3/h	10.638	11.810	12.980
wet gas for distribution	Nm^3/h	8360	9500	10.680
ethylene content in the gas	kg/h	2744	2744	2744
gas composition % weight/% volume:				
H_2		0,81/12,06	0,86/12,45	0,9/12,7
CH_4		13,94/25,91	15,24/27,35	18,3/28,5
C_2H_2		1,39/ 1,60	0,70/ 0,83	0,1/ 0,1
C_2H_4		25,81/27,20	23,23/23,85	21,2/21,2
C_2H_6		6,60/ 6,51	6,21/ 5,94	5,9/ 5,5
C_3H_6		15,00/10,60	17,60/12,04	19,7/13,3
C_3H_8		1,37/ 0,93	7,34/ 4,78	12,3/ 7,8
C_4		12,52/ 6,75	13,47/ 7,31	14,3/ 7,6
C_5 + w		22/58/ 8,54	15,35/ 5,45	9,4/ 3,3

Period II - TABLE III

		A	B	C
gasoline consumption	t/h	26,8	13,4	-
consumption of liquid gases	t/h	-	16,1	32,2
dry gas for distribution	Nm^3/h	23.000	27.230	31.500
wet gas for distribution	Nm^3/h	17.900	22.000	26.100
ethylene content in the gas	kg/h	5.960	5.960	5.960

gas composition % weight/% volume:

	A	B	C
H_2	0,81/12,06	0,93/13,24	1,01/14/05
CH_4	13,94/25,81	15,44/27,50	16,83/28,58
C_2H_2	1,39/ 1,60	0,67/ 0,72	0,13/ 0,14
C_2H_4	25,81/27,20	21,74/22,10	18,81/18,60
C_2H_6	6,60/ 6,51	6,32/ 6,00	6,13/ 5,66
C_3H_6	15,00/10,60	16,70/11,32	17,90/11,80
C_3H_8	1,37/ 0,93	11,30/ 7,32	18,57/11,70
C_4	12,52/ 6,75	12,62/ 6,80	12,70/ 6,65
C_{5+w}	22,58/ 8,54	13,28/ 5,00	8,22/ 2,82

REMARK: Figures in table III pertain to the period after increase of cracking facilities to four working furnaces, which is planned for 1968.

Calculation is based on data from the following sources:

CRP 1947 SCHUTT

KLIMIENKO, Ethylene production from gasoline and gases.

Opinion expressed by OBŁOJ on the BLACHOWNIA proposals:

Subject of this critique is a preliminary project for cracking of gasoline and gases at the BLACHOWNIA Cokery Plant which was prepared by the Projects and Construction Office of the KĘDZIERZYN Nitrogen Plant.

Basic assumptions for the project are:

Consumption and production figures:	Cracking of 69.600 tons of gasoline per year, plus 6700 tons per year of saturated hydro-carbons in gas form, ethane, and of higher order. Production of 20.400 tons of ethylene and 10.350 tons of propylene per year.
Installation:	2 pyrolitic furnaces with a processing capacity of 10 tons per hour of gasoline each, operating alternately; and one furnace for cracking of gases.
Investment cost:	36,5 million złotys.
Production cost:	According to the proposal, the technical cost to produce 1 ton of gases is 2287,8 złoty.

1. Raw Material

According to the proposal, the basic raw material for cracking is to be gasoline, with a boiling point between 50 and 150° C, in an amount of 60 000 tons per year, as well as gasoline used for cleaning purposes, with an approximate boiling point between 140 and 180° C. For the time being, the Authority for the PŁOCK Refinery has proposed to supply gasoline derived from "ropa romaszkinska" (ROMASHKIN crude oil) with the following approximate composition: (this data is based on gasoline supplied by the refinery in August 1963)

content of C - 85%
H_2 - 14.5%
S - 0.014%

bromine number 0.45; boiling point 44 - 150° C; density 0.710.

The large part of hydrogen makes this raw material particularly suitable for olefine cracking.

The cracking will occur in conditions allowing maximum yield of ethylene. Research work indicates that a maximum of ethylene is obtained from fraction of $C_7 - C_{10}$ aliphatic hydrocarbons. According to many other publications, the amounts of obtained olefines depend most of all on the group composition of the gasoline and on the conditions in which its cracking takes place; and to a lesser degree on the length of the hydrocarbon chain within the limits $C_5 - C_{15}$. In this case, the group composition of the gasoline is dictated by its derivation from ROMASHKIN oil. Fraction at an approx. boiling point between 90° and 180° C has the following group composition (according to CLT Nafta):

paraffine hydrocarbons	66 %
naphthenic "	22 %
aromatic "	12.1 %
olefine "	0.27 %

Possible small changes of the boiling point do not change the group composition in an appreciable way but, in case of an increase, affect adversely the sulphur content as demonstrated below:

Gasoline boiling between	35 - 159° C	contains	0.045 % sulphur
	140 - 198° C		ca 0.1 %
	183 - 230° C		ca 0.26 %
	221 - 263° C		ca 0.87 %

In case of a decrease, difficulties may arise in storing in Summer because of the large expansion of gasoline fumes. This expansion can be corrected by adding to the basic raw material gasoline used for cleaning purposes which has a boiling point between 140 - 180° C and which contains light hydrocarbons from the cracking.

In the opinion of the author the raw material is suitable for cracking.

The cracking of ethane, propane, and of butane derived from gasoline fraction constitutes a secondary process properly included to increase the yield of olefines, and for the economic operation of the installation. The author believes that the degree of conversion of gases assumed in the proposal has been chosen rather freely.

The cost of gasoline assumed in the proposal to be 1948 złoty per ton must be revised, in order to have it correspond to the cost of gasoline for cracking considered for other plants.

2. Technological Process and Equipment

The preliminary process is based on the cracking of gasoline in tube furnaces heated from the outside, of 2-zone construction, with a working period of 14 days between cleaning of tubes from coke by burning.

The cracking temperature in the proposal was accepted at 760° C, the average time 1.5 secs, and a 50% addition of steam. At these figures, the total ethylene yield was considered to amount to 29% of the feeding stock. A standard furnace of 10 tons of gasoline per hour consumption was proposed, corresponding to C.S.R.S. equipment.

Up to date technological processes for cracking of hydrocarbons presently used by Western countries are characterized by an ethylene yield on the 30% level, even without the cracking of additional gas hydrocarbons. These are mostly processes based on solid heat carriers - coarse-grained (TPC, Höchster-Koker); or fine-grained (LURGI); or in gas form (steam in the KELLOG Process).

Ethylene yields obtained at I.C.S.O. in ¼ of the technical installation with a fine-grained heat transfer agent from cracking of "ropa muchanowska" (MUKHANOV crude oil):

boiling point 140 - 242° C density 0.791

content of S = 0.06 %

C = 83.2 % of weight

H_2 = 12.5 % of weight

at a temperature of 780° C, at 100 % steam, 28 - 29.8 % of weight of the raw material, without secondary cracking of the remaining "alcaned" (?, alkylated?) gas hydrocarbons.

In the opinion of the author, the request for investments for the proposed process of cracking in tubes is well founded, even if this is an earlier process, industrially used in the USSR with equipment coordinated at C.S.R.S. It is suggested, however, to consider it a first step of operating over a period of 3 - 5 years and, after the first burning out of tubes in the cracking furnaces, to switch to a modern process with a higher yield of ethylene. The method will be worked out at I.C.S.O. and tested in an experimental and/or pilot installation which will be set up next to the industrial cracking facility with the possibility of shunting gases from the experimental installation into the production chain.

The cracking of gasolines at BLACHOWNIA will be ethylene-oriented. Scientific research work and results from experiments at I.C.S.O. indicate that for this process the proper temperatures are 760° - 830° C. Lowering of the cracking temperature causes a decrease in ethylene yield with a simultaneous increase of contents of olefines of higher order. An increase in temperature, on the other hand, raises considerably the acetylene portion in the cracked gas.

In view of the temperature of 760° C for the cracking of gasolines accepted in the proposal, the author suggests to provide for variable heating of the furnace which, at full production, would allow for a temperature of at least 780° C for the raw material in its radiation portion.

Addition of steam within the limits of 50 - 100 % of the gasoline will raise ethylene yield and decrease the amount of coke in the tubes.

Of advantage is also the reversing of part of the cracking gases and methane.

A test at I.C.S.O. of the cracking of gasoline fraction A_3 from "ropa romaszkinska", which has:

boiling point	180 - 230° C
density	0.798
content of sulphur	= 0.284 %
% CA	= 9.4
% CN	= 28.4
% Cp	= 62.4

provided the following yields on laboratory scale:

	at 760° C	at 800° C
ethylene	24 - 27 % of weight	24 - 29 % of weight
propylene	up to 14 %	10 - 11 %

This means that ethylene and propylene yields, as applied to the cracking of gas aliphates, have been assumed sufficiently high in the proposal, but the total amount of cracking gas has been figured too high.

The cracking gas column should be operating at 140 - 150° C, and not at 125° C.

Utilization of the heat inherent in the gases in the form of steam production for the cracking is sensible because it improves the thermal efficiency of the process.

De-sulphurization of the gases through the use of a cold NaOH solution , in the opinion of the author is not insufficient. A detailed analysis of this problem by the planner is suggested, particularly since in the proposal the distribution of sulphur in compounds was assumed rather freely.

The ethane fraction together with saturated gas hydrocarbons of a high order, will be cracked separately, and this process is to be based on a cracking temperature of 800 - 830° C.

With respect to the present-day level of technology, "idling" (no-work) operation of furnaces is a thing of the past. Possibilities should be explored to use the furnace during this period as a heater. The frequent extinguishing and lighting of a furnace is, in the opinion of the author, an even less advantageous solution, Cracking gases obtained directly in a "burned out" ("broken in?") furnace should be used for heating - if they contain oxygen.

3. Propylene and its utilization.

Utilization of ethylene obtained from cracking as well as from cokery gas for production of polyethylene and ethylene benzene has already been decided and provides no ground for objections.

The cracking of 69 600 tons per year of gasoline, according to the proposal, will provide 10 350 tons of propylene per year. Its economic utilization will influence, to a large degree, the economy of the production based on cracking gases. It should be utilized in conjunction with the small amount of propylene from cokery gas, if a polyethylene facility is going to be built in BLACHOWNIA.

In the belief of the author, it is correct to accept a max. 12 % of propylene per amount of raw material, that is 8350 tons per year. From cokery gas, 450 tons of C_3 per year; that is a total of 8800 tons per year.

Anticipated consumption is: 1000 tons for glycerine (laboratory//pilot installation), and 400 tons of copolymers. There remains a pool of 7400 tons of propylene per year. Its utilization has been rather widely discussed already.

Propylene should be processed in the form of a C_3 fraction in order to avoid expensive installations for concentrating and purification.

Other feasible and suggested alternatives for propylene utilization at BLACHOWNIA:

(1) glycerine synthesis (ca 7000 tons per year)
(2) propylene oxide and glycol
(3) butanol - by the oxo method
(4) isopropanol
(5) cumene, for further processing into phenol
(6) olefines C_6 - C_9, for processing into alcohols by the oxo method.

The author believes alternatives (5) and (6) to be the economically most advisable ones.

To produce glycerine in the proposed amount, the country is lacking hydrogen peroxide which is needed in an amount of 0.5 parts per part of glycerine. This process should be linked to the production of

H_2O_2 from isopropanol. Glycerine production is limited to the PŁOCK refinery (M.Z.R.iP.) in an amount of 10 000 tons per year.

For propylene oxide production, BLACHOWNIA lacks chloride needed in an amount of 1.6 ton Cl_2 per ton of propylene. The method of direct oxidization can be taken into consideration only after 1965. For butanol synthesis by the oxo method, BLACHOWNIA lacks CO + H_2 gas, whereas shipment of propylene to OŚWIĘCIM would present too many difficulties.

Isopropanol synthesis would present no difficulties as far as investments are concerned, and could be accomplished in a short time, but there is no demand in the country for 7500 tons of this alcohol per year.

Production of isopropyl benzene in an amount of 20 000 tons per year from the propylene pool (0.37 ton per ton) is technologically linked to the synthesis of ethylene benzene and can be done on a 30 - 50 % diluted fraction of propylene. It can be tied to the production of phenol in PŁOCK. But the authors of the proposal as well as the representatives of M.Z.R.iP. did not accept the suggested cooperation, motivating its refusal with technical difficulties in building a second installation for phenol in PŁOCK.

The author believes planning in this direction should be continued in case the size of ducts in the installation for phenol production should be changed, using the cumene method based on the Soviet process. This alternative would entail the building of one alkylator for cumene, in addition of alkylators for ethylene benzene, and increasing the distillation section for ethylene benzene with additional columns. Alkylation would occur in the presence of $AlCl_3$ by a propane-propylene fraction, with utilization of un-processed propane for cracking. In stead of benzene, cumene would be shipped to PŁOCK to increase phenol production - perhaps in the second stage.

The Planning and Construction Office of Z.K. KĘDZIERZYN has already calculated the cost for this alternative.

Synthesis of olefines $C_6 - C_9$ from propylene for further processing to oxo alcohols, in cooperation between Z.K.BLACHOWNIA and Z.Ch. OŚWIĘCIM, constitutes, in the author's opinion, another justified alternative for propylene utilization. In the oxo process these olefines can be converted into alcohols $C_7 - C_{10}$ which are useful in the production of softening agents for PCW plastification. Polymerization of 7400 tons of propylene will produce ca 6000 tons of olefines $C_6 - C_9$, which amounts to 5100 tons of oxo alcohols. In application, these alcohols will successfully substitute for 2 - ethyl hexyl alcohol produced in OŚWIĘCIM from carbide. The cost of production for this alcohol, based on prices from before 1 July 1960, is 17 632 złoty per ton. In England the price of 2 - ethyl hexanol is £ 210/- per ton, whereas the price of alcohols from oxo synthesis is £ 170/- per ton.

Propylene polymerization into olefines $C_6 - C_9$ with a phosphorus catalyst occurs in gentler conditions than tetramerization. By the end of 1965 I.C.S.O. will have worked out a process, including production requirements. This would make it possible to start synthesis of olefines $C_6 - C_9$ at BLACHOWNIA, and synthesis of aliphatic alcohols based on these olefines at OŚWIĘCIM, simultaneously in 1965. The author sees a possibility to shorten this time by obtaining data from the USA at the planned purchase of processes for the installation for propylene tetramerization for PŁOCK; or in cooperation with the DDR - where, at the Buna Works in SCHKOPAU, processes are in use for propylene polymerization to dodecylene.

Investments costs at BLACHOWNIA for this production are estimated by the author at ca 16 million złotys.

B.P.K. Z.A. KĘDZIERZYN, in cooperation with Z.Ch. OŚWIĘCIM should make a calculation for oxo alcohols based on propylene obtained from cracking at BLACHOWNIA, in combination with the calculation for 2 - ethyl hexanol, at prices which will be in force after 1 July 1963, in order to submit the two above alternatives for utilization of the propylene fraction at BLACHOWNIA to superior authorities for a decision.

4. Utilization of material remaining after cracking.

In the proposal, the amount of aromatic fraction after deduction of internal consumption was figured at 5800 tons per year, that is 8.3 % of the gasoline total, and 31 % of the total of liquid fractions. A decision for utilization of the aromatic fraction was postponed till after the installation starts to operate.

In ½ of technical tests of cracking gasoline from MUKHANOV crude oil, which were performed at I.C.S.O., the total amount of material remaining after cracking was about 30 % of the raw material. According to scientific publications, they amount to 35 - 40 % for heavy gasolines.

Chromatographic analysis of the fraction of post-cracking materials which boils at 150° C, and which in the proposal has been designated as "aromatic fraction", obtained at 780° C in a 3 secs period from cracking gasoline with a boiling temperature of 44 - 150° C, shows the following contents (on laboratory scale):

content of benzene	45.3 % of volume
toluene	38.9 %
xylenes	7.2 %
ethylene benzene	1.2 %
thiophene	1.4 %
octane	2.9 %
other	3.1 %

Also in a fraction boiling between 150 - 190° C, the content of aromatics is high: ca 80 %. In the opinion of the author, the most proper direction for utilization of fractions up to 150° C with a content as cited, or similar, is as a solvent for the lacquer industry. Experiments for this purpose will be conducted at the Institute for Paint and Lacquer. The liquid fraction is too poor in xylenes to warrant their extraction.

The remainder with a boiling point above 150° C which in the proposal was to be mixed with fuel oil used for heating of cracking furnaces, should be checked for utilization in soot production, in view of the probable high content of aromatics.

5. Investments outlays and production costs.

The author has no objections. A calculation in detail will be performed at PTR, in particular after receipt of exact prices from CSRR, and after the cost of the raw material from the CZECHOWICE refinery has been definitely determined.

6. Labor force.

In addition to the total of 17 people working in three shifts provided for in the proposal, the author deems it proper to add: 1 analyst for every shift and 1 control technician (who will also take care of the gas distribution section), that is a total of:

$$17 + 3 + 1.5 = 21.5 \text{ people.}$$

7. Automatic installation.

The author does not object to the proposal in the preliminary project. I believe that a master control panel facility would be desirable.

8. Storage of raw materials and gases.

In my opinion, a seven-day supply of basic raw material is insufficient. I suggest to keep a larger amount of gasoline in storage, at least a ten-day supply. The proposal does not contain storage tanks for ethylene, for the fraction C_3, nor for the fraction C_4.

9. Combining gas production with Z.A. KĘDZIERZYN.

The planned cooperation between Z.K. BLACHOWNIA and Z.A. KĘDZIERZYN, regarding gas production, for the alternative where the polyethylene facility is in KĘDZIERZYN, is generally well founded. Doubts arise regarding the balance of gases, since amounts of gases obtained are figured too high. A detailed analysis by PTR is also required of the problem of a second ethylene apparatus in view of the assumed ethylene level, to find out if it can be dropped in favor of feeding

80 - 85 % concentrated ethylene to an ethylene column.

10. Final suggestions.

The author proposes to approve the cracking of gasoline and gases as a preliminary project of the actual technical project which will have to be worked out - considering, however, remarks and suggestions made in par. 1,2,3,4,6, and 8.

It is considered necessary to have BPK calculate the synthesis of olefines $C_6 - C_9$, and to arrange for direct technical consultations with M.Z.R.iP. in PŁOCK in the matter of cooperation at the production of cumene; and with Z.Ch. OŚWIĘCIM in the matter of production of oxo alcohols.

BLACHOWNIA Śl., 30 September 1960.

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