OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

D00392

United Nations Industrial Development Organization

ID/WG.54/[illegible].Rev.1
11 February 1970
ORIGINAL: ENGLISH

PET.SYMP. 3/5

Interregional Symposium on the Petrochemical Industries in the Developing Countries

Baku, USSR, 21 - [illegible] October 1969

PROCESSES FOR THE PRODUCTION OF PETROCHEMICAL INTERMEDIATES 1/

by

H. Köfermann
H.K. Kampmann
W. Krönig
H. Linde
D. Reitz

presented by

[illegible]
Farbenfabriken [illegible] (Bayer)
[illegible]
Federal Republic of Germany

1/ The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

Distribution
LIMITED

ID/WG.34/20 SUMM
23 July 1969

ORIGINAL: ENGLISH

...l Nations Industrial Development Organization

...Regional Petrochemical Symposium on the
...lopment of the Petrochemical Industries
...veloping Countries

PET. SYMP. B/5

SUMMARY

PROCESS FOR THE PRODUCTION OF PETROCHEMICAL INTERMEDIATES 1/

by

H. Höfermann
H.K. Kamptner
W. Krönig
W. Kunde
O. Reitz

Farbenfabriken Bayer AG (Bayer)
Leverkusen
Federal Republic of Germany

Introduction

Of the many possibilities of converting basic petrochemical materials into intermediates, a group will be discussed here which has the following features in common:

(a) the under-mentioned simple aliphatic monoolefins serve as raw materials:

ethylene
propylene
butylenes

(b) these feedstocks are converted with the aid of molecular oxygen

---

1/ The views and opinions expressed in this paper are those of the authors and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

1. The ethylene oxide direct oxidation process (further development)

Since described at Teheran Hüls has made improvements in the process giving better yields, longer life of the catalysts, etc.

The ethylene is oxidized with air in the gas phase on a stationary silver catalyst at 250 - 350°C and increased pressure in two stages. The starting product ethylene and air are fed into the cycle of the first stage and are conveyed with the recycle gas by means of a compressor to the parallel-connected catalyst furnaces of the first stage. The heat of reaction is dissipated by the evaporation of water contained in the jacket space of the catalyst furnaces. The steam produced is utilized in the process. After appropriate cooling down, the furnace gas is passed on to a scrubber, where the ethylene oxide obtained is washed out with water. The gas free from ethylene oxide is replenished again with ethylene and air and is subjected again to the process just described. Part of the washed gas is passed to the catalyst furnaces of the second stage where furnace gas is also washed with water in a scrubber belonging to the second stage and is then passed into the atmosphere. The ethylene oxide formed is separated from the washing water, and the latter is again used for washing. The content of carbon dioxide and acetaldehyde in the ethylene oxide is reduced down to slight traces by fine distillation.

The production of one metric ton of ethylene oxide requires 1,720kg of ethylene; the investment for a plant for the production of 90,000 metric tons of ethylene oxide per year amounts to about 16.5 million US$.

2. Oxidation of ethylene to acetaldehyde and of propylene to acetone

Also in these processes, molecular oxygen is added on to the olefinic double bond, but in this case not with the formation of an epoxide, but with the formation of an aldehyde or ketone. The reaction is not carried out here - like in 1. - in heterogeneous catalysis in the gas phase, but the oxygen addition takes place with the aid of a redox system:

(a) The olefins are oxidized by palladium salts (palladium chloride) in aqueous solution with reduction of the palladium chloride to metal.

(b) The palladium metal is again converted into palladium chloride by cupric chloride with reduction of the cupric chloride to the cuprous chloride.

(c) The cuprous chloride is oxidized again by oxygen to the cupric chloride.

The reaction can be carried out either as a single stage or as a two stage process. In the first the ethylene and oxygen are passed into a vertical reactor containing the catalyst solution, regeneration of the catalyst taking place continuously. In the second, air is used to regenerate the catalyst in a separate reactor and the oxidation of ethylene carried out with air. In both cases the reaction takes place under moderate pressure and at 100°C which is sufficient to evaporate and concentrate the acetaldehyde which is then purified by a two-stage distillation.

The production of one metric ton of acetaldehyde requires 760 kg of ethylene (93.5% yield); the investment for a plant for the production of 70,000 metric tons of acetaldehyde per year amounts to about 4.0 million US $.

Acetone process

Propylene and catalyst solution are fed to a continuous reactor system in which virtually the entire propylene is converted in "one single through-put". The reaction takes place at a low pressure and about 100°C. After pressure reduction has taken place, the acetone is stripped off from the catalyst solution. The latter is treated with air and recycled into the reactor system. The crude acetone thus obtained is purified by means of a two-stage distillation. The air used for the oxidation is almost completely freed from oxygen.

The production of one metric ton of acetone requires 700 kg of propylene (yield 91 %); the investment for a plant for the production of 24,000 metric tons of acetone per year amounts to about 3.5 million US $.

The above mentioned processes of catalytic direct oxidation of olefins are applied in numerous large-scale plants all over the world. The aldehyde process has already reached the 2.5 thousand million lbs/year total capacity mark.

3. Addition of acetic acid on to ethylene by oxidative dehydrogenation to vinyl acetate

Till recently, vinyl acetate has been produced from acetylene and acetic acid. The recent trend to ethylene as a basic material has led to the development of a synthetic method based on ethylene, acetic acid and oxygen.

(a) In the Wacker method, the palladium salt catalytic route is used by which acetaldehyde is obtained as a co-product.
Ethylene and oxygen are reacted at 120 - 130°C and a pressure of 30 - 40 kg/cm^2 in the presence of the catalyst dissolved in aqueous acetic acid. The molar ratio of acetaldehyde to vinyl acetate can be varied within a range from 0.3 to 2.5.
The production of one metric ton of vinyl acetate and a molar ration of acetaldehyde to vinyl acetate of 1.13 requires 845 kg of ethylene; the investment for a plant for the production of 75,000 metric tons of vinyl acetate per year and 43,000 metric tons of acetaldehyde per year (molar ratio acetaldehyde to vinyl acetate 1.13) amounts to about 7.10 million US $.

(b) In the Bayer method, ethylene and oxygen are recycled through a vapouriser in which they pick up acetic acid vapour. Fresh oxygen is added and the gaseous mixture passed at 140 - 250°C and 5 - 10 kg/cm^2 gauge over a metallic noble metal catalyst.
The plants according to the Bayer process in operation, under construction or in planning have together a vinyl acetate capacity of more than a quarter million metric tons per year.

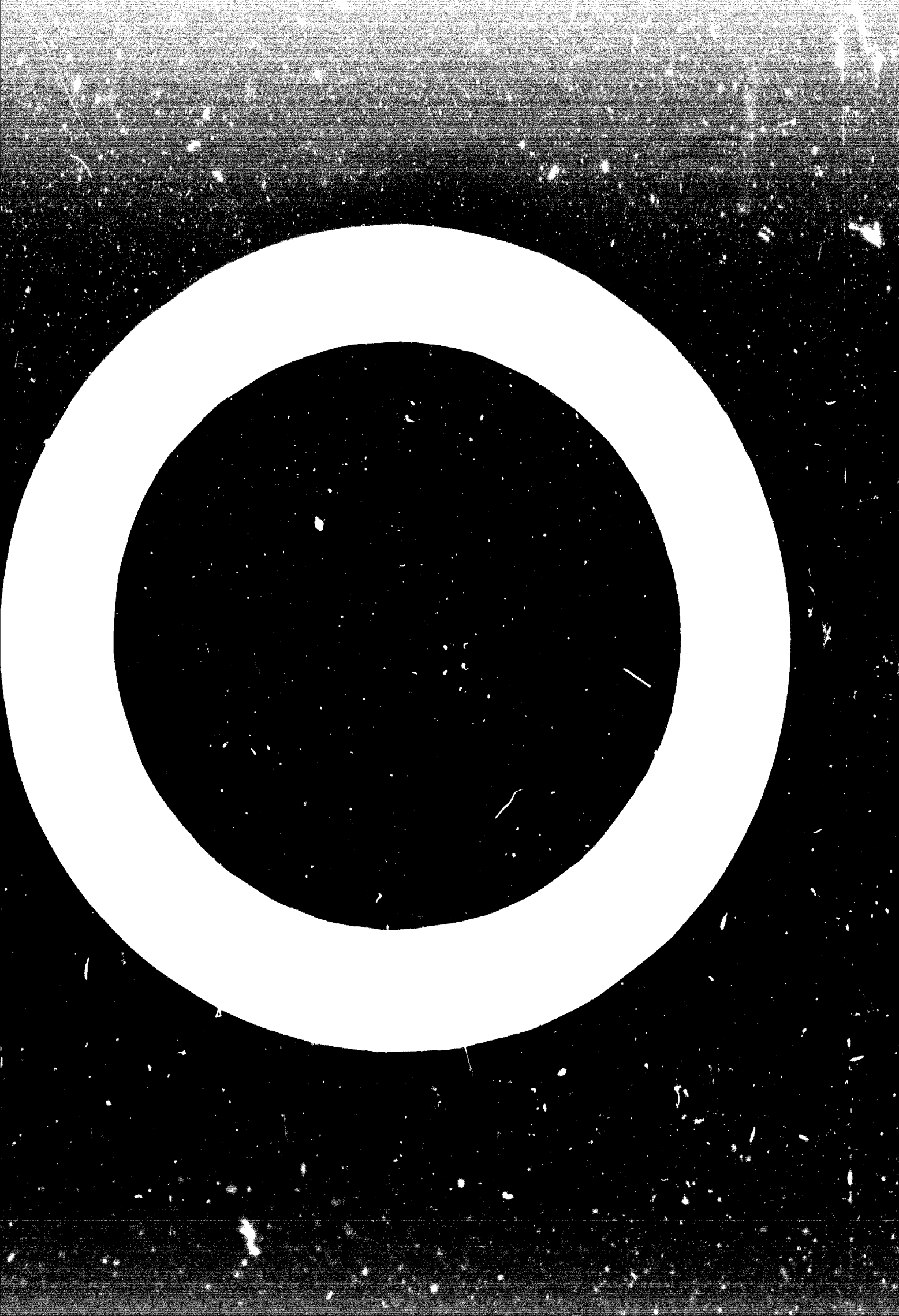
4. Oxidative splitting of n-butene to acetic acid

Difficulties in the oxidative splitting of n-butene to acetic acid due to the formation of by-products have been overcome by the preliminary formation of butyl acetate. Oxy-acetoxylation then gives acetic acid.

Feedstock is the n-butene mixture (with butane), as it is received from the foregoing treatments. The conversion of the n-butene with glacial acetic acid (first stage) is accomplished in the liquid phase at elevated temperature and pressure in the presence of a finely divided catalyst,

suspended in the reaction mixture and recycled in the system. The non-converted butene (20 - 50%) can - if so desired - be recycled via an extractive distillation. The butyl acetate in the acetic acid solution is oxidized (second stage) with air at elevated temperature and pressure in liquid phase with high recycle inside the system of the liquid reaction products through a heat exchanger. The energy of the residual gas is used for the compression of the air.

The production of one metric ton of acetic acid requires 800 kg of n-butene; the investment for a plant for the production of 60,000 metric tons of acetic acid per year amounts to about 10 million US$.



1.0 Ethylene oxide direct oxidation process

2.0 Oxidation of ethylene to acetaldehyde and of propylene to acetone

2.02 Reaction scheme

2.10 Acetaldehyde process

2.11 One-stage process

2.111 Description of the process

2.12 Two-stage process

2.121 Description of the process

2.101 Production

2.20 Acetone Process

2.21 Description of the process

2.03 Technical plants

3.0 Addition of acetic acid on to ethylene by oxidative dehydrogenation to vinyl acetate

3.01 Principle of vinyl acetate synthesis from ethylene

3.10 Procedure with palladium salt / redox system in the liquid phase

3.11 Description of the process

3.20 Procedure in heterogeneous catalysis

3.21 Description of the process

3.23 Technical plants

4.0 Oxidative splitting of n-butene to acetic acid

4.01 Fundamentals

4.02 Description of the process

Introduction:

Of the many possibilities of converting basic petrochemical materials into intermediates, a group will be discussed here which has the following features in common:

a) the under-mentioned simple aliphatic monoolefins

serve as feedstocks:

ethylene

propylene

n-butene

b) these feedstocks are converted with the aid of molecular oxygen.

The examples mentioned here show at the same time the versatility in the designing of the chemical action when the basic materials are converted into intermediates.

The following subjects will be dealt with more specifically:

1.0 Addition of oxygen to ethylene to form ethylene oxide

The traditional production of ethylene oxide was a typically chemical method of operation: Hypochlorous acid - produced from chlorine and water - was added on to ethylene to form ethylene chlorohydrin, which was then reacted with a base - for example lime - to ethylene oxide and calcium chloride.

It was a great step when this method of operation of classical chemistry was replaced by the petrochemical method of operation of direct addition of molecular oxygen on to the double bond of ethylene in heterogeneous catalysis, ethylene oxide being formed. Hüls reported on this at the 1964 Petrochemistry Meeting.

It has now repeatedly been found that the petrochemical processes can still be substantially improved. Thus, also the process of Hüls has been much improved during these five years, and Hüls now submitted a report on the present state.

Addition of oxygen to ethylene to form acetaldehyde, and to propylene to form acetone

Also in these processes, molecular oxygen is added on to the olefinic double bond, but in this case not with the formation of an epoxide, but with the formation of an aldehyde or a ketone. The reaction is not carried out here - like in 1.0 - in heterogeneous catalysis in the gas phase, but the oxygen addition takes place with the aid of a redox system.

2.1 Conversion of ethylene into acetaldehyde

This process was already basically reported on by Hoechst during the previous UNIDO Petrochemistry Conference. It appears advisable now to give a survey of the present state of the process.

2.2 Conversion of [illegible] into acetone

Transferring the method of operation of the acetaldehyde process to propylene as a feedstock leads to the formation of acetone. As this process too has in the meantime gained real technical importance, it appears advisable to give a report on it.

3.0 Addition of acetic acid to ethylene in oxidative substitution to the vinyl series

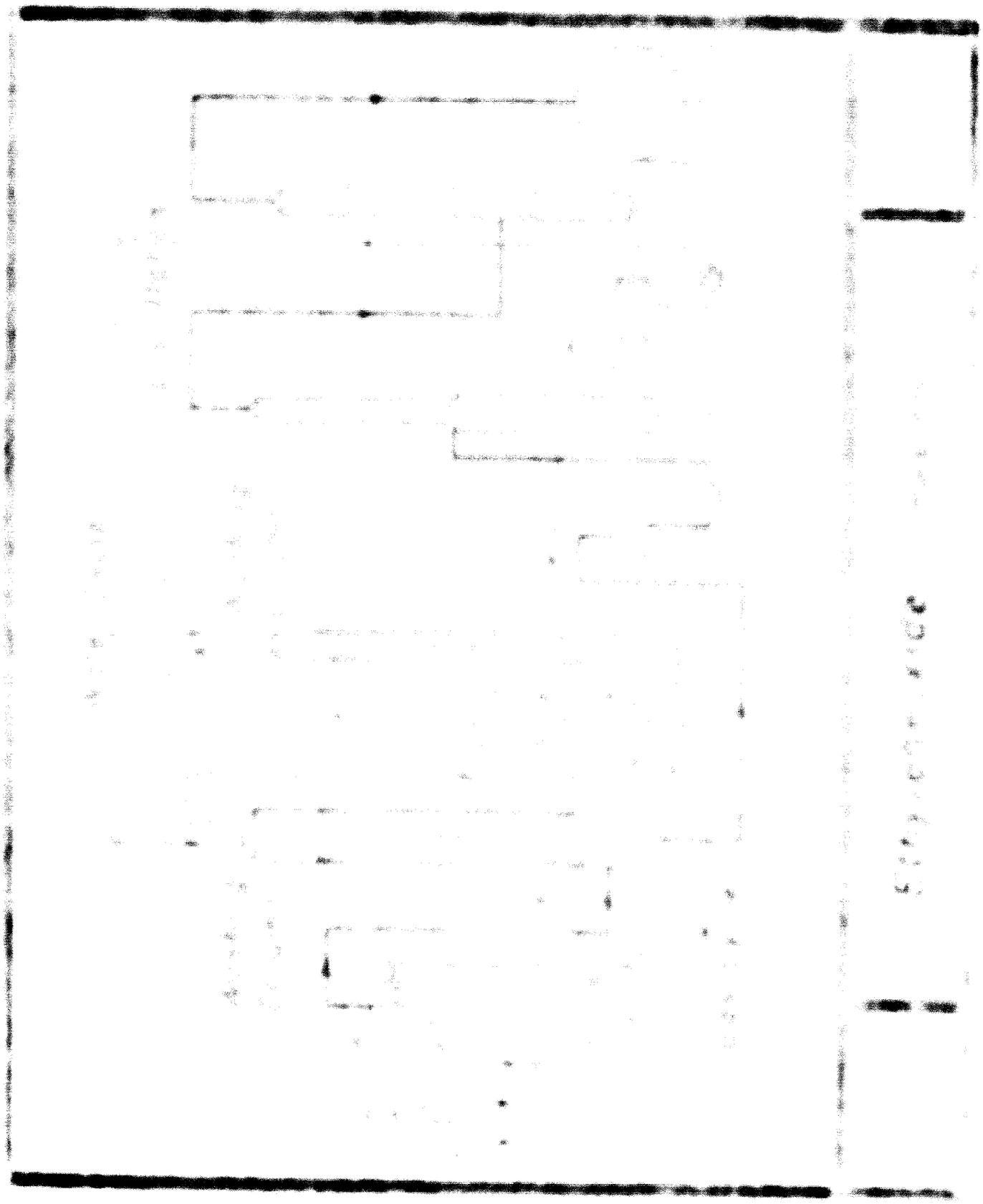
In the processes considered so far (1.0 and 2.0), the molecular oxygen added on to the olefin with elimination of the double bond. In the process to be considered now, the oxygen does not add on to the double bond, but it causes an oxidising dehydrogenation with formation of water, so that the unsaturated ester vinyl acetate is obtained, with the double bond being maintained.

Two methods of operation will be considered here:

3.1 In the process of Hoechst, the conversion takes place, like in the acetaldehyde process, with the aid of a redox system; besides vinyl acetate, also acetaldehyde is obtained;

3.2 in the process of Bayer, the oxidising dehydrogenation is carried

out in heterogeneous catalysis; no acetaldehyde is being formed.



plants. In this process the oxidizing agent is either air or pure oxygen. The use of air or oxygen is an economic question and depends on the [illegible] plant.

As far as [illegible] is concerned, there has been no change [illegible] principle of the ethylene oxide [illegible] stationary silver catalyst, [illegible] from 230°C to [illegible] of the ethylene [illegible] Most process [illegible] stages, [illegible] primary, as well as improvements of the [illegible] flow to conversion, [illegible] considerable [illegible] the specific conversion figures [illegible] for [illegible] plant [illegible] additional [illegible] (or ethylene oxide [illegible] ppm).

[illegible]

In [illegible] as shown in the diagram, [illegible] by catalytic [illegible] The starting [illegible] the first stage [illegible] by the use of a compressor [illegible] The [illegible] to the required

by-product carbon dioxide is highly exothermal. The heat of reaction is dissipated by the evaporation of water contained in the jacket space of the catalyst furnaces. The steam produced is utilized in the process. After appropriate cooling [illegible], the formed gas is passed on to a scrubber, where the ethylene oxide obtained is washed out with water. The gas free from ethylene oxide is replenished anew with ethylene and air and is subjected again to the process just described. Part of the washed gas is passed to the catalyst furnaces of the second stage whose furnaces are also washed with water as the above mentioned is the second one and to them passed into the atmosphere. The ethylene oxide formed is separated from the [illegible] water, and the latter is again used for washing. The content of carbon dioxide and acetaldehyde in the ethylene oxide is [illegible] slight traces by fine distillation.

4.0) Consumption figures

a) Raw material consumption per metric ton of ethylene oxide

ethylene (1.5 kg/cm² absolute) 1020 kg

Air (6 kg/cm² absolute) 7000 m³ at S.T.P.

b) Utilities consumption per metric ton of ethylene oxide

cooling water (20° C) 360 m³

cold water (+ 5° C entry) 13 m³

(+15° C exit

power (500 v)	150 kwh
power (6 kv)	500 kwh
demineralized water	12 m^3
steam (20 kg/cm^2 absolute)	4.9 tons
steam (4 kg/cm^2 absolute)	0.4 ton
Credit:	
steam (50 kg/cm^2 absolute)	8 tons
steam condensate	5.3 tons

c) Investment — for a 30,000 metric ton per year plant about 10.5 million US $ (in the Federal Republic of Germany) battery limits (without store for starting and finished products, first catalyst filling, engineering, financing, site development, lines up to the battery limits)

d) Personnel required — 5 - 6 workmen per shift

1.04 Literature

Publication in the supplement volume of Ullmann is being prepared.

2.0 Oxidation of ethylene to acetaldehyde and of propylene to acetone

2.01 Fundamentals

At the 1964 UNIDO Petrochemical Meeting, Hoechst reported on the production of acetaldehyde by oxidation of ethylene. The reaction dealt with at that

time is not restricted to the oxidation of ethylene, but can be applied more generally. Besides the oxidation of ethylene to acetaldehyde (2.1), also the oxidation of propylene to acetone (2.2) will therefore be dealt with here.

The reaction principle is the use of 4 redox systems:

a) The olefin is oxidized by palladium salts (palladium chloride) in aqueous solution with reduction of the palladium chloride to the metal.

b) The palladium metal is converted again by means of cupric chloride into palladium chloride with reduction of the cupric chloride to cuprous chloride.

c) The cuprous chloride is oxidized again by oxygen to form cupric chloride.

These three steps, supplemented by the summary d), are shown by the following scheme (2.01):

a) $R\text{-}CH = CH_2 + PdCl_2 + H_2O \longrightarrow R\text{-}CO\text{-}CH_3 + Pd + 2\ HCl$

b) $Pd + 2\ CuCl_2 \longrightarrow PdCl_2 + 2\ CuCl$

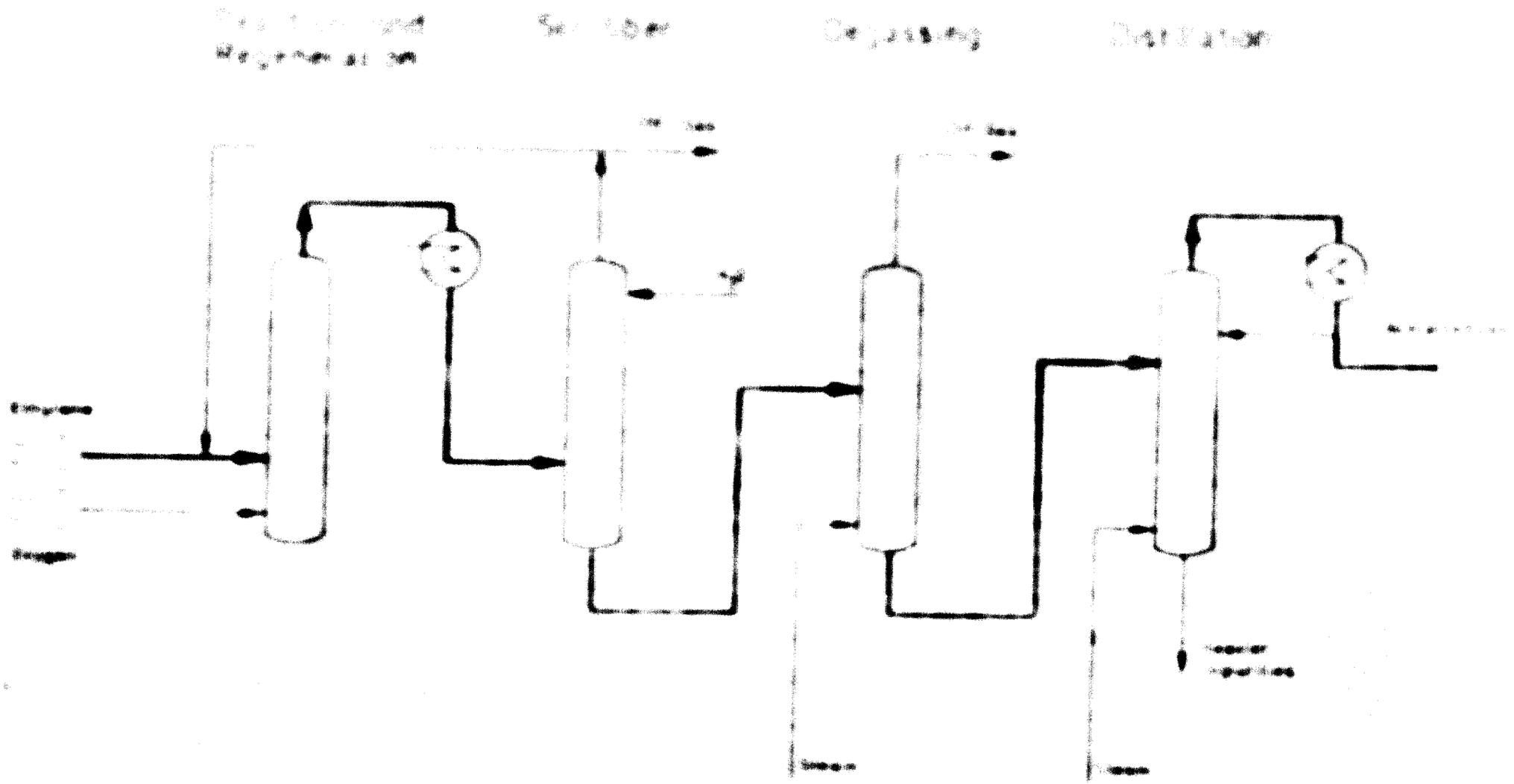
c) $2\ CuCl + 2\ HCl + 1/2\ O_2 \longrightarrow 2\ CuCl_2 + H_2O$

d) $R\text{-}CH = CH_2 + 1/2\ O_2 \xrightarrow{PdCl_2,\ CuCl_2} R\text{-}CO\text{-}CH_3$

$R = H,\ CH_3,\ C_2H_5$

2.02 Reaction scheme of olefin oxidation to aldehyde or ketone

[illegible]



2111 | ACETALDEHYDE PROCESS (ONE STAGE)

2.12 Two-stage process

2.121 Description of the process

[illegible] catalyst solution are passed through a continuously operating reactor in which virtually the entire ethylene is converted in the course of one throughput. The reaction takes place under [illegible] at about 130°C. The heat of reaction obtained is used for the purpose of concentrating the acetaldehyde [illegible] by pressure reduction.

The [illegible] catalyst solution is regenerated in a second reactor by air [illegible] at about the same temperature as in the first reactor. The crude acetaldehyde is purified by two-stage distillation.

The [illegible] catalyst solution is almost completely freed from the [illegible] for other purposes. The first reactor is almost completely [illegible] degree of purity of the [illegible] can be taken down to 95 %.

The [illegible] almost identical with that [illegible] acetaldehyde, and the [illegible] from it, also [illegible].

2.122 Quantities involved

[illegible] are related to the ethylene used.

When raw and auxiliary materials according to the following specification are used for the production of one metric ton of acetaldehyde (99.6 %) the average consumption for the one-stage and the two-stage process is:

	One-stage process	Two-stage process
a) Raw materials		
Ethylene (100 %)	670 kg	670 kg
Oxygen (100 %)	280 m³ at S.T.P.	
Air	–	1000 m³ at S.T.P.
Hydrochloric acid (31 %)	15 kg	40 kg
Palladium	approx. 1.5 g	1.5 g
Iron rings	0.5 m³	–
b) Auxiliaries		
Cooling water (20° C)	20 m³	40 m³
Boiler water (12° C)	7 m³	10 m³
Steam	1200 kg	1500 kg
Power	40 kwh	100 kwh

c) Personnel required (both one-stage and two-stage process)

1 engineer

1 foreman

1 laboratory assistant

4 workers per shift

d) Investment

For a plant for the production of 10,000 metric tons per year

of acetaldehyde, the investment, based on Federal Republic of Germany, is about 4.0 million US$. The investment comprises the overall performances inside battery limits. This amount includes in the case of the one-stage process the oxygen plant and in the case of the two-stage process the air compressors.

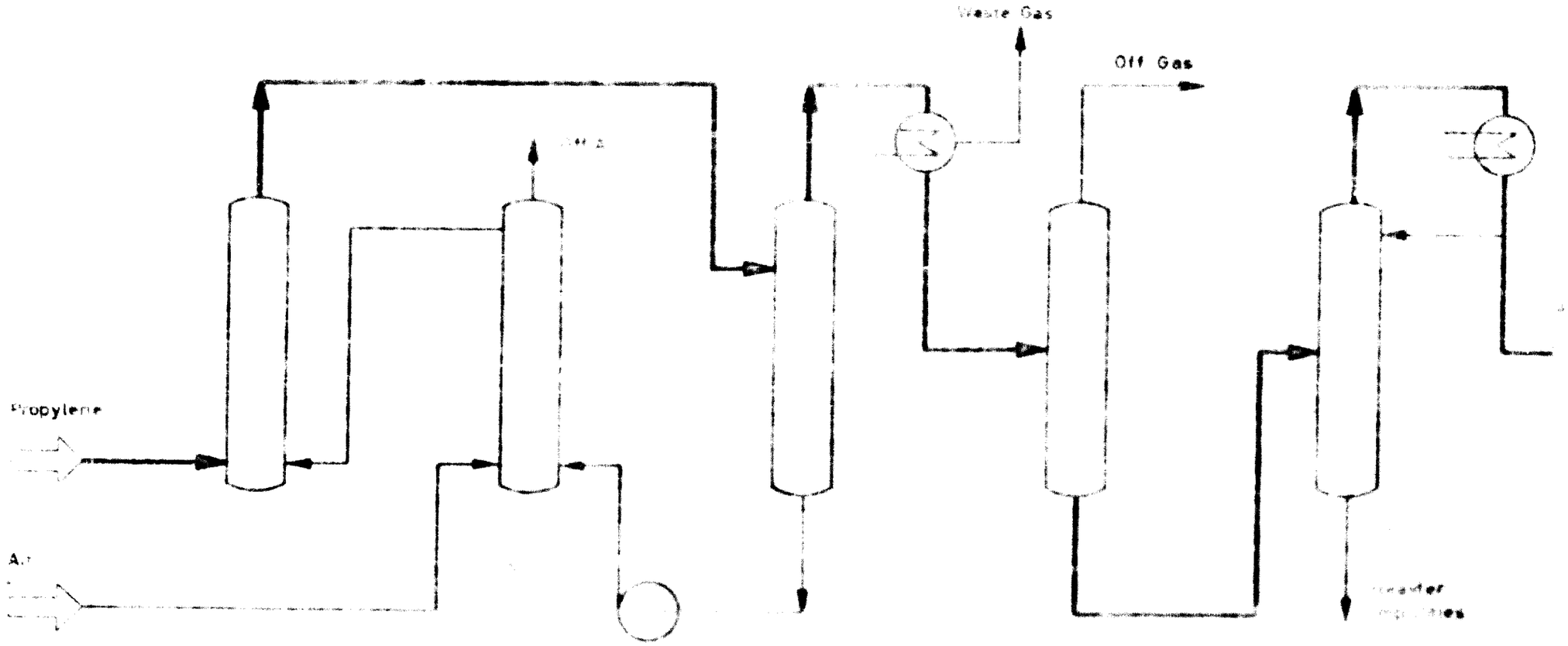
2.103 Technical plants

2.104 A number of improvements of the various operational steps have been made since 1959, when the first aldehyde plant by the process of direct oxidation of ethylene came on stream. While in 1960 the capacity per reactor was 24,000 metric tons per year of acetaldehyde, it rose in 1963 to 40,000 metric tons per year, and in 1965 a plant was built with 50,000 metric tons per year of acetaldehyde capacity per reactor. Latest plants of 100,000 metric tons per year of acetaldehyde are being planned.

2.20 Acetone synthesis

2.21 Description of the process (see Scheme 2.21)

Propylene and catalyst solution are fed to a continuous reactor system in which virtually the entire propylene is converted in "one single operation". The reaction takes place at a low pressure of about 10 atm. The reaction is exothermal and its heat effect is 71 kcal per mol of acetone produced. After pressure reduction has taken place, the acetone is stripped off from the catalyst solution. The latter is treated with air and recycled into the reactor system. The crude acetone thus obtained is puri-


Waste Gas
Off Gas
Propylene
Air
Reaction
Regeneration
Crude Acetone Separation
Degassing
Final Distillation

[illegible] process is carried out, [illegible] obtained, as a heterogeneous cata- [illegible] catalysts, preferably in the gas [illegible]

[illegible] described in more detail below:

[illegible] liquid [illegible]

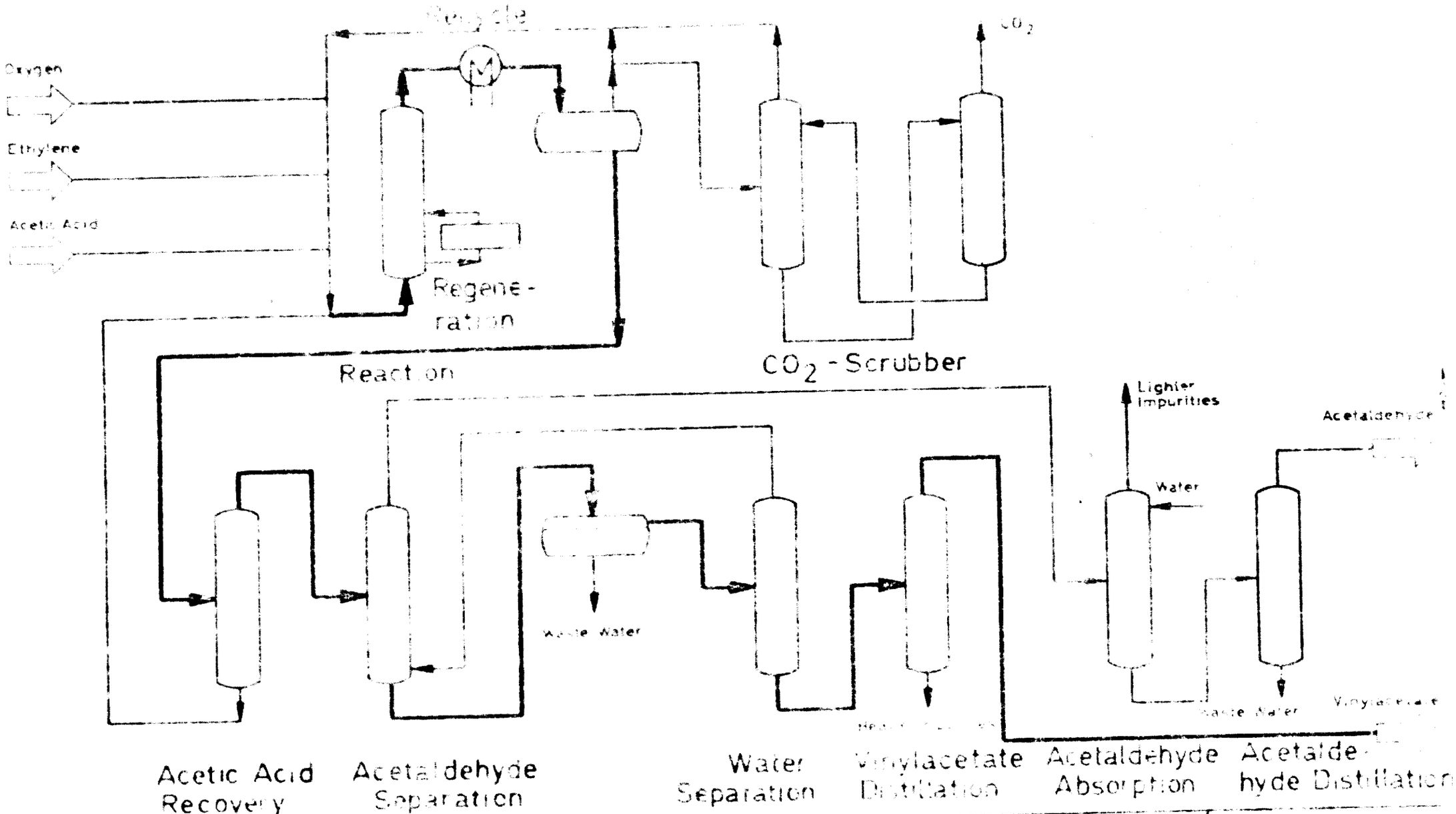
[illegible] 3.11)

[illegible] in which the [illegible] reaction [illegible] temperature [illegible] reaction [illegible] carbonate [illegible], acetic acid, [illegible] separated from [illegible] acetic acid [illegible]

[illegible] can be varied [illegible].

[illegible]

[illegible] vinyl acetate (70.5 %) and a [illegible] of 1.13 [illegible]



3.11 VINYLACETATE - PROCESS (LIQUID PHASE HOECHST)

a) Raw materials:

Ethylene (100 %)	845 kg
Oxygen (100 %)	760 kg
Catalyst, chemicals	3.75 US$

b) Utilities

Cooling water	593 m³
Low-pressure steam	2.62 tons
High-pressure steam	2.90 tons
Power	315 kWh

c) Personnel required

1 Chemist

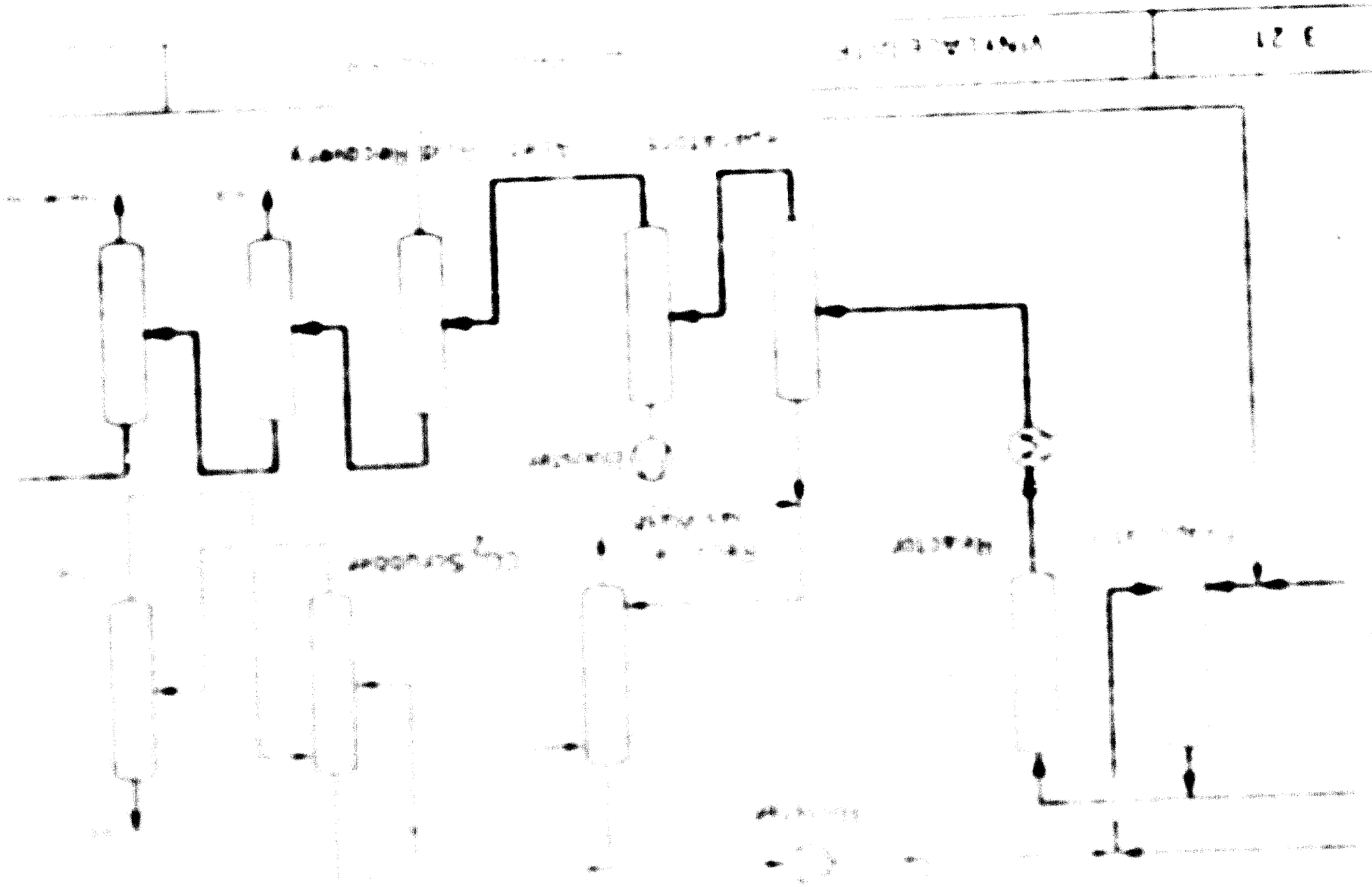
1 Foreman

6 Workmen per shift

The above data include already the consumption figure for the acetic acid plant.

d) Investment

The investment for the erection of a plant for the production of 75,000 metric tons per year of vinyl acetate with simultaneous production of 43,000 metric tons per year of acetaldehyde (molar ratio acetaldehyde to vinyl acetate 0.57) is 7.19 million US$ based on the Federal Republic of Germany. This amount includes all expenditures for machinery and equipment including assembly inside battery limits. The acetaldehyde produced as a co-product in a molar ratio of 1.13 is oxidized to form acetic acid. The



[illegible] the reclaimability of the acetic acid contained in the waste water [illegible] water formed in the process is [illegible] a waste water containing [illegible], in particular ethylacetate. The vinyl [illegible]

[illegible] by Hoechst acquired a license on this [illegible] jointly developed the process to operational [illegible] pilot plant experiments were later [illegible].

[illegible] a second will come [illegible] fifth plant [illegible] on-stream until early in 1971.

[illegible] together a vinyl acetate capacity of more than [illegible] tons per year.

[illegible]

2. [illegible] Proc. 7th World Petr. Congr. Vol. 5, 41/49 (1967)

3. [illegible] 40/48 (1968)

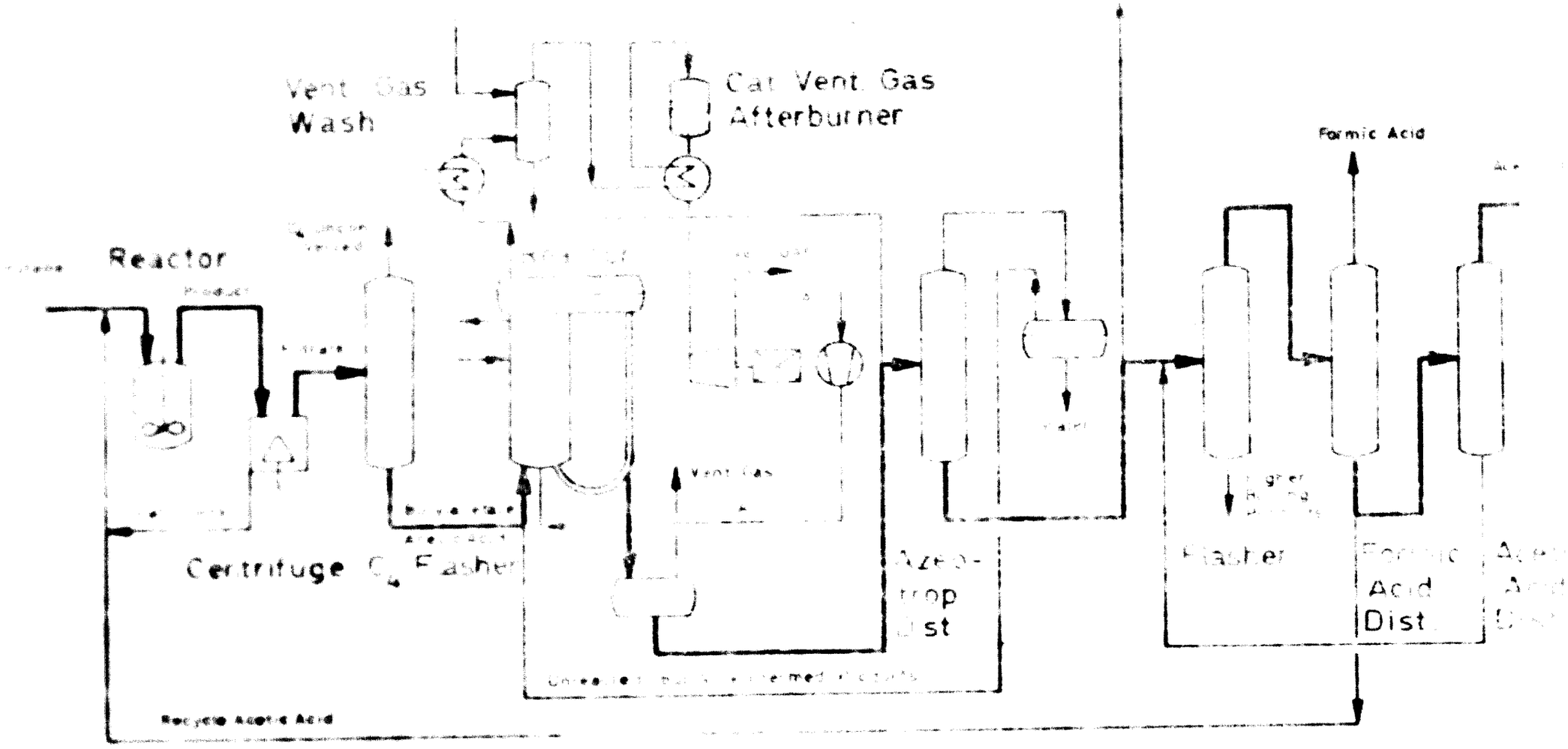
4. [illegible] 33, 771/774 (1968)

5. [illegible] Chemistry and Industry (1956), 1509/1513

4.01 Reaction

4.02 Reaction mixture

Reaction of the gaseous mixture (with butane), as it is received from the foregoing operation. The conversion of the n-butane with surplus acetic acid (first stage) is accomplished in the liquid phase at elevated temperature and pressure in the presence of a finely divided catalyst, a



Stage I
Formation of Sec Butylacetate

Stage II
Oxidation of Butylacetate to Acetic Acid (Oxidative Cracking)

Distillation of Oxidation Products to Pure Acetic Acid

suspended in the reaction mixture and recycled in the system. The non-converted butene (20--50 %) can - if so desired - be recycled via an extractive distillation. The butyl acetate in the acetic acid solution is oxidized (in one stage) with air at elevated temperature and pressure in liquid phase with high recycle ratios the system of the liquid reaction products through a heat exchanger. The energy of the residual gas is used for the compression of the air.

The recovery of the pure acetic acid from the liquid oxidation products is carried out by azeotropic and normal distillation; it is possible - if wanted - to recover also the intermediate: sec. butyl acetate.

4.2 Technical data

Technical data for the acetic acid production by this process are as follows:

Stage	I	II
Reaction temperature °C	110	195
Pressure atm	280	550

Raw materials and utilities (for 1 metric ton of acetic acid)	Unit	per 1 metric ton of acetic acid product
butene	kg	800
power	kwh	670
cooling water	m³	156
condensate	kg	1,350
steam (20 atü) production (product from waste heat)	kg	1,280

Acetic acid production m.t./yr	25,000	60,000
Total investment million DM.	6.125	10.0

Erdöl Kohle, Erdgas Petrochem. 5, 445/55 (1967)

Hydrocarbon Process. 47, 140/146 (1968)

Conclusion

The ethylene which is available or n-butene available are rather small. It is advantageous to have a process for converting the ethylene chemical (acetic acid) for which often a rather large market.

Summary

Up to now the basis of petrochemical conversion of basic materials [illegible] the simple basis of the action of oxygen on gaseous hydrocarbons to produce one of the broad width of variations [illegible] reactions. The introduction of these methods of [illegible] would enable us to be rich fruit.


25. 1. 72