THE HYDROGENATION
OF
HYDROXY COMPOUNDS

A Thesis submitted in fulfilment of the
requirements for the Degree of Doctor of
Philosophy in the Faculty of Science of
the University of Glasgow

by

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- CONTENTS -

Page

SECTION 1 - Introduction

Chapter 1. General Introduction.......... 1.

Chapter 2. Previous Work................. 8.

Chapter 3. Thermodynamical considerations of the contemplated reactions.. 14.

Chapter 4. Factors affecting the rate of a hydrogenation reaction....... 24.

(1) The catalyst.................... 24.

(2) The stirring.................... 29.

(3) The temperature................. 32.

(4) The pressure.................... 35.

SECTION 11 - Apparatus Used.

Chapter 5. The autoclave................. 37.

(1) The design of the autoclave....... 37.

(2) Criticism of the autoclave design. 46.

(3) The testing of the autoclave...... 58.

(4) The operation of the autoclave.... 61.

Chapter 6. Examination of the Products.... 63.

(1) Gaseous........................... 63.

(a) The Macfarlane.............. 63.

(b) The Bone and Wheeler......... 65.

(c) The Podbielniak Unit......... 68.

Page

(2) Liquid.......................... 75.

<u>SECTION 111 - Experimental</u>.

Chapter 7. Preliminary work.............. 82.

- (1) The hydrogenation of ethylene glycol.......................... 82.
- (2) The pyrolysis of ethylene glycol... 84.

Chapter 8. The pyrolysis of glycols....... 88.

- (1) Previous work...................... 88.
- (2) Pyrolysis of ethylene glycol
  - (a) Vapour phase................ 94.
  - (b) Liquid phase................ 100.
- (3) Pyrolysis of 1,2-propylene glycol.. 105.
- (4) Pyrolysis of 2,3-butylene glycol... 109.
- (5) Conclusions........................ 111.

Chapter 9. The hydrogenation of glycols above their decomposition temperature.................. 113.

- (1) Ethylene glycol.................... 113.
- (2) 1,2-Propylene glycol............... 117.
- (3) 2,3-Butylene glycol................ 119.
- (4) Conclusions........................ 121.

Chapter 10. The testing of catalysts and the preparation of an active catalyst.................... 124.

Chapter 11. The hydrogenation of olive oil in the autoclave............. 141.

Chapter 12. The hydrogenation of alpha glycols below the temperature of violent decomposition...... 154.

Page

(1) Ethylene glycol.................. 154.

(2) 1,2-Propylene glycol............. 160.

(3) 2,3-Butylene glycol.............. 162.

Chapter 13. The vapour phase hydrogenation of ethylene glycol........... 163.

Chapter 14. The hydrogenation and pyrolysis of glycerol......... 165.

(1) Previous work.................... 165.

(2) Pyrolysis of glycerol............ 169.

(3) The hydrogenation of glycerol.... 173.

(4) Conclusions...................... 176.

Chapter 15. Hydrogenation and pyrolysis of laevulose.................... 177.

(1) The pyrolysis.................... 178.

(2) The hydrogenation................ 180.

SECTION lV - Conclusions.

Chapter 16. Conclusions.................. 184.

Chapter 17. Suggestions for future work... 190.

SECTION V - Addenda.

Chapter 18. The amended design of a high pressure plant................ 193.

ILLUSTRATIONS.

(1) The Apparatus Used

(a) The High Pressure Plant.

(i) The autoclave gland (Fig. 3).... 39.

(ii) Lens ring joint. (Fig. 4)....... 42.

(iii) High pressure union joint (Fig. 5)...... 43.

(iv) I.C.I. valve. (Fig. 6).......... 44.

(v) The autoclave gland. (Fig.8)..... 47.

(vi) The oil bottle fastened to the side of the autoclave cubicle (Fig. 12a)...................... 56.

(vii) The testing of the autoclave (Fig. 13)...................... 59.

(viii) The autoclave showing the effect of corrosion. 29/3/38. (Fig. 14)...................... 60.

(ix) The chain stirrer. (Fig. 12).... 55.

(x) The paddle stirrer.............. 145.

(xi) The chain stirrer (Fig.30a)..... 146.

(xii) Layout of the autoclave for stirring by means of bubbling hydrogen through the liquid. (Fig. 31)...................... 149.

(xiii) The autoclave showing support for stirring gear. (Fig. 32)..... 151

(b)/

(b) Suggested Designs for High Pressure Plant

(i) Suggested design of a gland by Andreas Hofer. (Fig. 9)......... 49.

(ii) Design of a gland in three parts. (Fig. 10)................ 52.

(iii) Design of a gland with spring in place of a lantern ring. (Fig. 11)...................... 53.

(iv) Design of autoclave stirrer shaft (Fig. 36)................ 194.

(v) Design for a high speed stirrer (Fig. 37)...................... 200.

(c) Apparatus Used in Certain Pyrolysis Reactions at Atmospheric Pressure.

(i) Apparatus used in vapour phase Pyrolyses. (Fig. 25)........... 102.

(d) Gas Analysis Units.

(i) The Macfarlane gas analysis Unit (Fig. 15).................. 63.

(ii) The Bone and Wheeler unit (Fig. 16)...................... 65.

(iii) The Podbielniak unit. (Fig. 17)...................... 68.

(iv) Graph of Podbielniak results (Fig. 18)...................... 69.

(v) Condensing train for Podbielniak apparatus (Fig. 19)............ 70.

(e) Liquid Analysis Units.

(i) Fractionating column (1) (Fig.20) 75.

(ii)/

(ii) Fractionating column (2) (Fig. 21)........................ 77.

(iii) Fractionating column (3) (Fig. 22)........................ 78.

(iv) Fractionating column, general view, (Fig. 22a)................. 78.

(v) View of top of column. (Fig.23).. 80.

(2) The Catalyst.

(i) The surface of a nickel catalyst (Fig. 2)......................... 24.

(ii) Bubbler used in the measurement of catalytic activity. (Fig.29)... 129.

(iii) Graph showing the effect of the number of washings on the alkali content of a catalyst. (Fig.30)... 137.

(3) Conditions during Autoclave Reactions (Graphs)

(a) Hydrogenations.

(i) Ethylene glycol (from previous work) (Fig. 1)..................... 13.

(ii) Ethylene glycol over Raney nickel (Fig. 24)................... 81.

(iii) Ethylene glycol over nickel on kieselguhr.(Fig. 26.).............. 115.

(iv) 1,2, Propylene glycol (Fig.27)... 117.

(v) 2,3, Butylene glycol (Fig. 28).... 119.

(vi)/

(vi) Hydrogenation of glycerol

1. (Fig. 34a).................. 173

2. (Fig. 34b).................. 173

3. (Fig. 34c).................. 173

(b) Pyrolyses

(i) Glycerol over Raney nickel. (Fig. 33)........................ 170

BLUE-PRINTS.

Three blue-prints will be found in a pocket at the back of this thesis. They are as follows:-

(1) The Autoclave assembly as it was at the outset of this work.

(2) A suggested design for an autoclave showing various modifications.

(3) A suggested design for the layout of the autoclave cubicle showing changes in the drive for the stirrer shaft and form and position of the oil bottle.

BIBLIOGRAPHY.

The following books have been consulted throughout this work:-

Design and Construction of High pressure Plant.

"The Design, Construction, and Operation of a High Pressure Chemical Plant" a Ph. D. Thesis by John F.C. Gartshore, Glasgow. 1936.

"Design and Construction of High Pressure Chemical Plant", by Harold Tongue.

Hydrogenation and Pyrolysis Reactions.

"Unit Processes in Organic Synthesis" by Groggins.

"The Hydrogenation of Organic Substances" by Ellis.

"The Pyrolysis of Carbon Compounds" by Hurd.

Catalysis.

"Catalysis and its Industrial Applications", by Maxted.

Thermodynamical Considerations.

"The Free Energies of some Organic Compounds" by Parks and Huffmann.

ABBREVIATIONS.

The following abbreviations have been used throughout this work:-

Ann.

Justus Liebig's Annalen der Chemie.

Bull, Soc. Chim.

Bulletin de la Société chimique de France.

Bull. Inst. Phys. Chem. Res. Japan.

Bulletin of the Institute of Physical Chemical Research. Japan.

Compt. Rend.

Comptes Rendus lebdomadaires des Séances de l'Académie de Sciences.

Chem. Abst.

British Chemical Abstracts.

Chem. Ztg.

Chemiker Zeitung.

Chem. Zentr.	Chemisches Zentralblatt.
Helv. Chim. Acta.	Helvetica Chimica Acta.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
J.A.C.S. or Trans. Amer. Chem. Soc.	Journal of the American Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Russ. Phys. Chem.	Journal of the Russian Physical Chemical Society
J. Pract. Chem.	Journal fur practische Chemie.
Proc. Roy. Soc.	Proceedings of the Royal Society.

T.I.C.E.

Transactions of the Institute of Chemical Engineers.

SECTION I.

INTRODUCTION.

CHAPTER

1.

INTRODUCTION.

The reduction of an organic compound may be accomplished in a number of ways of which the following are the most well known:-

(1) By the action of a metal upon an acid or alkaline solution or suspension of the compound.

(2) By the action of an alkali metal on an aqueous or alcoholic solution of the compound.

These methods have been known and used both in laboratories and in industry for many years. More recently, however, it has been shown that certain types of compound can be reduced by means of molecular or gaseous hydrogen in the presence of a catalyst. This process is called "Hydrogenation".

The reduction of a compound by hydrogenation possesses certain advantages over the two older methods described above.

Firstly it is possible by this means to prepare compounds which are practically unobtainable by any other means, or which were previously unknown. For example, hexa-hydro-benzene may be obtained by passing/

passing the vapour of benzene mixed with hydrogen over a nickel catalyst, whereas it is almost impossible to prepare it otherwise. Again, the preparation of the esters of the higher saturated fatty acids is practically impossible unless by hydrogenation.

Secondly, a hydrogenation process will normally yield a purer product in that hydrogen, the substance to be hydrogenated, and a solid catalyst are the only raw materials, and the product is thus less likely to be contaminated with acids, alkalis, or the salts of base metals which are used or formed during the process.

Hydrogenation processes can readily be operated on a continuous, instead of a batch, process, thus allowing of a considerable saving in plant and personnel.

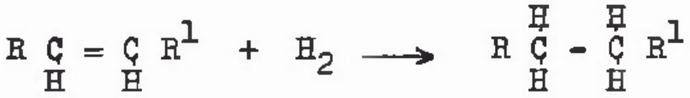
The earliest technical application of hydrogenation reactions was the reduction of the double bond occurring in liquid fats. The fat was thereby hardened or converted to the glyceride of the saturated fatty acid. Such hardened fats are commercially much more valuable than the liquid fats from which they are made.

More recently, in 1925, methanol began to be prepared by the hydrogenation of carbon monoxide over a catalyst under considerable pressures, and today this industry supplies most of the methyl alcohol of commerce. The process has also been extended to the preparation of motor fuels from water gas, enabling those countries without natural oil resources to produce liquid fuels from the raw materials, coal, water, and air. The most successful of these is the well known Fischer-Tropsch process.

Hydrogenation of petroleum products is carried out in those countries which have an abundance of natural oil. For example, it is claimed that the essential qualities of lubricating oil can be improved by suitable hydrogenation.

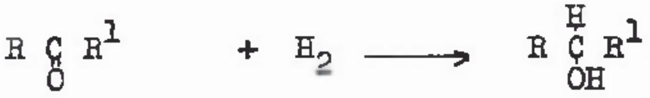
There are three main types of hydrogenation reaction

(1) Reduction of an ethylene linkage.



$$R\underset{H}{C}=\underset{H}{C}R^1 + H_2 \longrightarrow R\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}R^1$$

(2) Reduction of a carbonyl to an alcohol group



$$R\underset{O}{C}R^1 + H_2 \longrightarrow R\overset{H}{\underset{OH}{C}}R^1$$

(3) Hydrogenolysis, or those reactions which involve the breaking up of the molecule hydrogenated. The rupture may only involve the splitting off of water e/g.

$$RCOOR^1 + H_2 \longrightarrow RCH(OH)R^1 + H_2O$$

or there may be an actual breaking of a bond between two carbon atoms

The reduction of a compound containing a hydroxyl group is therefore "hydrogenolysis".

$$R.OH + H_2 \longrightarrow RH + H_2O$$

Reductions of this type are, however, well known although they usually require much more rigourous conditions than the reduction of a compound containing a double bond. For example, ethyl/

ethyl ether can be hydrogenated to a mixture of ethane and ethyl alcohol by passing its vapour and hydrogen over nickel at 250°C (Sabatier and Senderens Bull Soc Chim 33, 1905, 616.)

$$C_2H_5OC_2H_5 + H_2 = C_2H_5OH + C_2H_6$$

The number of reported hydrogenations of hydroxy compounds is small, however, being confined mainly to hydrogenations of unsaturated alcohols, the unsaturated linkage being reduced while the hydroxyl group remains unchanged. It is thus possible to reduce allyl alcohol to propyl alcohol over nickel at 130°C. (Sabatier, Comptes Rends, 144, 879, 1907). When an aromatic alcohol is hydrogenated, at low temperatures, reduction is confined almost exclusively to the benzene nucleus, cinnamic alcohol being reduced to cyclo-hexyl propanol at 25 - 50°C and 2 - 3 atmospheres pressures in the presence of platinum catalysts. (Waser Helv. Chim. Acta. 1925, 8, 117). Phenols may suffer hydrogenation either in the nucleus to form cyclohexanols/

cyclohexanols (Brochet, Bull. Soc. Chim. 1914, 15, 588.) or the hydroxyl group may be hydrogenated to form an aromatic hydrocarbon (Kling and Florentin, Comptes Rends, 1927, 184, 885.)

On the other hand, alcohols figure largely as the end products of various hydrogenations. Ketones, esters and acids may all be hydrogenated to give alcohols.

(Covert and Adkins J. A. C. S. 54, 4117, 1932.
Falkers and Adkins J. A. C. S. 54, 1146, 1932, and J. A. C. S. 53, 1096, 1931.)

It would seem then that the reduction of a hydroxyl group by direct hydrogenation is an operation which has so far escaped the attention of research workers and it was thought that with the plant available in the College, it might be possible to attack the problem and open up a comparatively new field of research. The particular branch chosen was the hydrogenation of the poly-hydroxy compounds in that, at the time at which the work was commenced, they seemed to hold out more promise of positive results.

CHAPTER

II.

PREVIOUS WORK ON THE HYDROGENATION OF HYDROXY COMPOUNDS.

As has been previously stated, the number of reported hydrogenations of hydroxy compounds is small. Indeed, no case of the hydrogenation of a purely aliphatic primary alcohol to a hydrocarbon has been noted. It has been shown, however, that if the alcohol is partly aromatic, hydrogenation can be effected both in the benzene ring and in the hydroxyl group. Benzyl alcohol may thus be reduced to toluene by passing the vapour mixed with hydrogen over nickel at 375°C and atmospheric pressure (Sabatier and Senderens BUll. Soc Chim. 33, 616, 1905,). It is also well known that phenols can be hydrogenated to hydrocarbons at 70 - 80 ats pressure and 180°C over alumina.

When the alcohol contains two hydroxyl groups, reduction of one of these can be effected in certain cases. For example, 1, 3, propylene glycol may be hydrogenated to n. propyl alcohol by the use of a copper chromite catalyst in the liquid phase/

phase at 250°C and 175 ats pressure.

$$CH_2OH-CH_2-CH_2OH + H_2 = C_2H_5-CH_2OH + H_2O$$

1,3, Butylene glycol may also be hydrogenated under similar conditions to n.butyl and sec. butyl alcohol (Connor and Adkins. J.Am. Chem. Soc., 54, 4678, 1932).

The hexose sugars may be catalytically reduced to the corresponding alcohols. Glucose and laevulose for example can be hydrogenated to mannitol and sorbitol at 130°C and 100 ats pressure with a nickel oxide catalyst. (Ipatieff Chem. Abst., 1913, 7, 1171.) This hydrogenation, however, is important only so far as the first stage in the reduction of the sugars. Under more severe conditions; glucose, sorbitol, mannitol, sucrose, lactose, and maltose can be hydrogenated to give varying amounts of methyl alcohol, propylene glycol and 4 hydroxy - 2 alpha hydroxy methyl furane. The catalyst used is of the copper-chromium variety and the reaction is carried out at 300 ats pressure and a temperature of 250°C (Zartman and Adkins

J.A.C.S./

J.A.C.S. 1933, 55, 4559).

Dupont de Nemours (U.S.P. 196, 3997 - 196, 4001), also states that it is possible to prepare glycols by heating a polyhydric alcohol with hydrogen and a copper chromite catalyst at not below 200°C and 2,000 lbs. per sq. inch. For example it is possible to hydrogenate sorbitol to give a 33% yield of 1,2, propylene glycol.

It has been further shown that sugars, starch, cellulose, glycerol, glyconic aldehyde and cyclic poly-hydroxy compounds may be hydrogenated by treatment with activated hydrogen in the presence of a catalyst at 70 - 100 atmospheres pressure and at temperatures ranging from 190 - 300°C. Glycerol and 1,2, propylene glycol form the main products. (I,G, Farbenhind. British patent 299,373. Oct. 24th 1927).

More recently, R. Yoshukowa and S. Hani (Bull. Inst. Phys. Chem. Res. Japan. 1938, 17, 1262.) have shown that hexitols are obtained by the hydrogenation/

hydrogenation of glucose at 70 - 120°C or of sucrose and starch at 160 - 180°C and 80 - 300 atmospheres pressure. If the temperature is increased to 190 - 240°C, propylene glycol, glycerol, ethylene glycol, ethyl alcohol and methyl alcohol are formed.

This review of the literature seems to indicate that

(1) The hydrogenation of a primary aliphatic alcohol of low molecular weight has not yet been accomplished.

(2) If the molecular weight of the alcohol is increased by the addition of a benzene ring, the hydroxyl group may be reduced.

(3) If two or more hydroxyl groups are present in a compound on non-adjacent carbon atoms, one of the hydroxyl groups can be hydrogenated, leaving an alcohol.

(4) If more than two hydroxyl groups are present on adjacent carbon atoms, hydrogenation yields a glycol with two hydroxyl groups on adjacent carbon atoms/

atoms.

(5) No record of the hydrogenation of a glycol having hydroxyl groups on adjacent carbon atoms has yet been recorded in the literature.

In view of this, an attempt was made in the College to hydrogenate ethylene glycol using Raney nickel as a catalyst. These attempts showed that a reaction took place between ethylene glycol and hydrogen in the presence of Raney nickel catalyst in the autoclave at 1500 lbs. per sq. inch and at a temperature of 237°C. (Private communication from J. Angus Esq.)

In this experiment the charge in the autoclave was

150 ccs. Ethylene glycol.
5 grams Raney nickel
Hydrogen to 1,000 lbs. per sq.inch.

The figure below (fig. 1) shows the conditions in the autoclave during the reaction. It is to be noted that a marked rise in pressure occurred when the temperature reached 200°C.

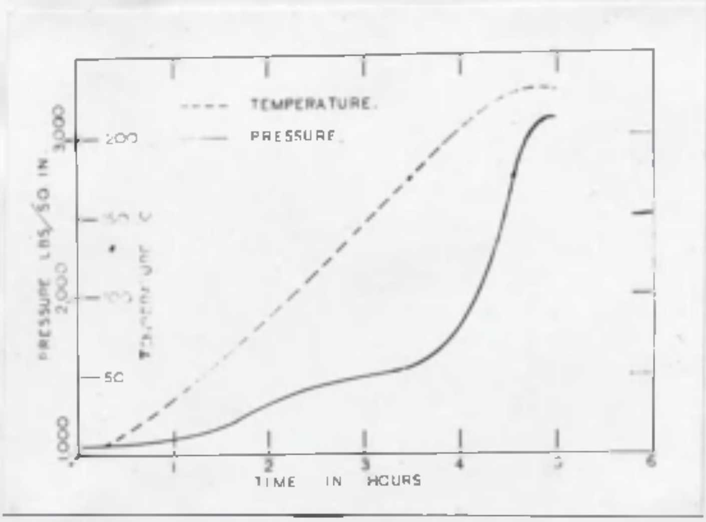


Fig. 1.

Autoclave conditions during hydrogenation of ethylene glycol.

The liquid products of the reaction were water, methyl alcohol, and formic acid. The gas from the reaction contained:-

Oxygen	0.7%
Nitrogen	1.0%
Carbon dioxide	20.3%
Hydrogen	13.0%
Methane	57.5%
Ethane and higher	7.5%

It was this reaction that the author set out to investigate and to extend, if possible, to the higher glycols and the sugars.

CHAPTER

III

THERMODYNAMICAL CONSIDERATION OF THE CONTEMPLATED REACTIONS.

Before commencement of the experimental work, a thorough investigation was made into the thermodynamics of the reaction in order to ascertain whether the reactions involved were theoretically possible. This was done by comparing the free energies of the compounds involved, since the free, or available, energy change in any reaction is a measure of the chemical forces or affinities involved.

The free energy of a compound may be taken as the amount of energy which is absorbed in the formation of the compound from its elements. Since we are concerned with differences in free energy only, it is convenient to assume that each element has zero energy at N.T.P. If the free energy of a compound (usually written DF) has a large negative value i.e. a considerable amount of energy is liberated in its formation, the compound may be formed from its elements.

Thus for the formation of a molecule of water from its elements at 25°C, DF = - 56,560 cals, and/

and the reaction once started proceeds vigorously to completion. Conversely if DF is positive i.e. energy is absorbed in the synthesis of a compound, that compound cannot be formed from its elements unless there is a degradation of a third compound, or other forms of energy are supplied For example, DF for acetylene is +55,160 cals i.e. 55,160 cals of useful work is absorbed in the formation of this gas from its elements, and from a consideration of the thermodynamical data, it should be impossible to synthesise this gas. This is found to be the case at room temperatures.

This thermodynamical reasoning may be carried a stage further to consider the reaction between two compounds. If, in such a reaction, there is a decrease in the free energy content of the constituents as we proceed from left to right, that reaction is thermodynamically possible. For example the hydrogenation of carbon monoxide may be written:-

$$CO_2 + 3H_2 \longrightarrow CH_4 + H_2O$$

Free energies (-40,500) (0) (-4,500) (-50,000)

$\therefore$ Change in free energy $= -4,500 + (-50,000) - (-40,500)$

$= -14,000$ cals

The/

The above reaction is therefore thermodynamically possible.

If, however, there is an increase in the free energy content of the constituents as in the reaction below, that reaction is thermodynamically impossible and cannot proceed under any conditions.

$$CH_4 \quad + \quad H_2O \quad = \quad CH_3OH \quad + H_2$$

Free Energies -4,500 - 50,000 - 26,000 (0)

Change in free energy = -26,000 -(50,000) - (-4,500)

= + 28,500 cals.

Where there is little or no change in the free energy content of the reactants, then these will exist together in equilibrium with each other.

Let us consider the reduction of a primary aliphatic alcohol to a hydrocarbon

$$R.OH + H_2 = RH + H_2O$$

We find that at 100°C the change in free energy is negative when R in the above equation contains from one to five carbon atoms. The hydrogenation is therefore thermodynamically possible in these cases.

[illegible]

No. of atoms in R.	ΔF (alcohol) cals.	ΔF (hydrocarbon) cals.
1	-26,020	-4,[illegible]
2	+14,000	+2,100
3	-3,0[illegible]	+19,[illegible]
4	+1,000	[illegible]
5	+18,[illegible]	[illegible]

100°C

No. of C atoms in R.	DF (alcohol) cals	DF (hydrocarbon) cals	Change in Free Energy
1	-36,500	-11,000	-25,000
2	-36,000	- 8,000	-22,000
3	-33,000	- 4,000	-11,000
4	-32,000	-1,000	-19,000
5	-25,000	-2,500	-27,000

Increasing the temperature to 500°C does not alter this general relationship. Indeed, as will be seen from the table below, the free energy change is in most cases greater.

500°C

No. of C atoms in R.	DF (alcohol) cals	DF (hydrocarbon) cals	Change in Free Energy
1	-26,000	-4,500	-28,000
2	-14,000	+8,000	-28,000
3	-3,000	+19,500	-28,000
4	+4,000	+30,000	-24,000
5	+15,000	+40,000	-25,000

The hydrogenation of a compound containing a hydroxyl group to a hydrocarbon is thus a thermodynamic possibility as far as the simpler members are concerned.

Let us now consider the hydrogenation of the poly-hydroxy compounds. The table below gives the change in free energy for the reduction of poly-hydroxy compounds to the corresponding primary alcohol or hydrocarbon.

Hydroxy compound	Change in free energy on reduction (cals)	
	To alcohol	To hydrocarbon
Ethylene glycol	-14,500	-15,100
Glycerol	-51,000	-67,000
Erithritol	-61,000	-83,000
Mannitol	-43,000	-69,000
Glucose	not known	-121,000

The above figures are all calculated for room temperature (15°C) although in no case has any attempt been made to hydrogenate any of these compounds at such a low temperature. Insufficient data is available to determine the change in free energy/

energy at temperatures nearer those used in practice. However, these figures show that the reactions are possible at a specific temperature, and it must be left for experiment to determine the optimum conditions.

Having determined that any reaction is thermodynamically possible, we may proceed a stage further and determine the equilibrium constant for the reaction by means of the formula

$$-DF = 4.57 \ T \ \mathrm{Log}K$$

where K is the equilibrium constant with the products appearing in the numerator and the reactants in the denominator, and T is the absolute temperature.

Considering the hydrogenation of ethylene glycol at 15°C to ethyl alcohol we get

$$C_2H_6O_2 + H_2 = C_2H_5OH + H_2O$$

$$+ 14{,}500 = 4.57 \times 268 \times \mathrm{Log}K$$

$$\mathrm{Log}K = 12.8$$

$$K = 3.6 \times 10^5$$

Thus the quantity of ethylene glycol vapour and hydrogen present if the system were in equilibrium is/

is negligible compared with the products. It should be remembered, however, that this calculation is made on the basis of the free energy change at 15°C, although such a reaction would be impossible in practice.

Finally it must be pointed out that thermodynamic possibility is no guarantee of chemical possibility, as either the reaction may proceed so slowly, even in the presence of a catalyst, that the products are not present in estimable quantities after considerable periods, or else the reaction may take an undesirable course so that the desired products are swamped by by-products. For example, the experiments on the hydrogenation of ethylene glycol have shown that above a certain temperature, decomposition proceeds to a far greater extent than the desired hydrogenation.

In/

In the above calculations, the following free energies were used

Substance	Free Energy (cals)		Authority
	At 100°C	At 500°C	
Methyl alcohol	-36,500	-26,000	Groggins
Ethyl alcohol	-36,000	-14,000	"Unit Processes
n Propyl alcohol	-33,000	- 3,000	in Organic
n Butyl alcohol	-32,000	+ 4,000	Synthesis"
N Amyl alcohol	-25,000	+ 15,000	
Methane	-11,000	- 4,500	
Ethane	- 8,000	+ 8,000	
n Propane	-4,000	+ 19,500	"
n Butane	-1,000	+ 30,000	
n Pentane	-2,500	+ 40,000	"

Substance	Free energy (15°C) Cals	Authority
Methyl alcohol	-39,960	Parks & Huffman "Free Energies of Some Organic Compounds"
Ethyl alcohol	-40,900	
n Propyl alcohol	-40,900	
n Butyl alcohol	-40,400	
n Amyl alcohol	-39,000	
Ethylene glycol	-80,200	
Glycerol	-113,600	
Erithritol	-149,400	
Mannitol	-222,200	
Glucose	-215,800	
Hexane	+ 3,000	
Water	- 56,560	
Water (100°C)	-56,600	
Water (500°C)	-50,000	

CHAPTER

IV

FACTORS AFFECTING THE RATE OF A HYDROGENATION REACTION.

(1) The catalyst used.

The catalyst used is of paramount importance in determining the speed of a chemical reaction. The following points have been considered.

Taylor (Proc. Roy. Soc. 1925, 108, 105.) has put forward a conception of a catalyst surface based on the fact that, as can be shown by X ray analysis, hydrogenation catalysts possess a definite lattice or crystalline structure. It is therefore postulated that a catalyst has a structure and surface as shown in the sketch below (fig. 2)

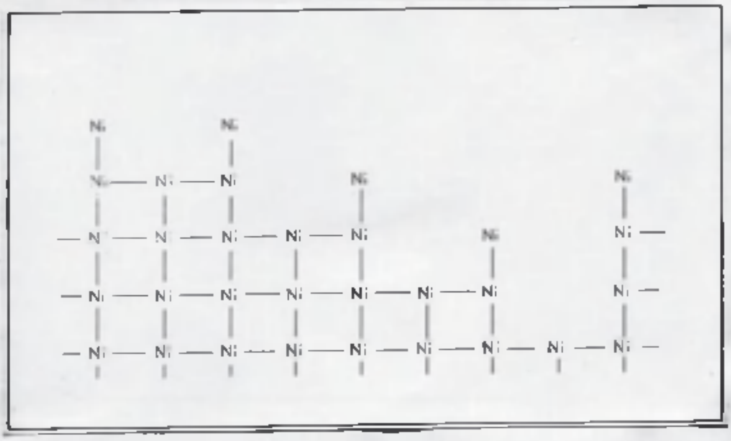


Fig. 2.

The surface of a nickel catalyst.

Nickel atoms are here shown thrust irregularly above the normal surface of the metal. These excrescences correspond to the active particles and are the seat of catalytic activity.

This theory affords us a general explanation of

(1) The importance of an irregular surface.

(2) The effect of excessive heat which sinters the catalyst and destroys these excrescences.

(3) The action of catalyst poisons which are attracted to and blanket off the excrescences from further action.

These nickel atoms which protrude from the parent metal and which have thus their chemical affinities to a large extent free, will exert an attraction on other unsaturated molecules. Armstrong and Hilditch (Proc. Roy. Soc 1925, 108, 113) have further pointed out that this attraction is mutual and is strong enough to loosen the nickel atom from the surface of the catalyst. It has been observed for example, that when a metallic vessel has been used for some time on the hydrogenation/

hydrogenation of liquids, the interior invariably becomes plated with a thin coating of nickel. Again the roughening observed when relatively smooth platinum is used as a catalyst in gas reactions is evidence of the actual migration of atoms from one place to another.

The preparation of such a surface was at one time performed almost exclusively by the reduction of metallic oxides. This reduction was carried out at as low a temperature as possible in order to minimise the sintering affect referred to above. It was further found that when the metallic oxide or carbonate was supported on an inert material such as pumice or kieselguhr, reduction could be carried out at a higher temperature without destroying the catalyst surface. This is probably due to the fact that at no point is there any marked concentration of nickel so that excrescences are less liable to be attracted back to the parent metal.

Recently a nickel catalyst has been prepared by Raney (Trans Amer. Chem. Soc. 54,4116, 1932/

1932) in which the necessary surface is obtained by leaching out the nickel from a nickel aluminium alloy by means of caustic soda. The preparation of this catalyst from the alloy does not require temperatures of over 100°C so that in this case there is no possibility of sintering with a consequent reduction in activity.

The alloy from which the catalyst is made should contain 50% or less nickel and is really a mixture of $NiAl_2$ and $NiAl_3$ together with excess nickel or aluminium depending upon the conditions (J Aubrey, Bull. Soc. Chim. 1938, 5, 1333, -8). X-ray studies of the alloy have been made before and after leaching(Nature 1938, 141, 1055,) and it has been shown that the alloy possesses a definite crystalline structure consisting of a face centred lattice having the aluminium atoms at the corners of the structure (Nature 1938, 141, 1055). The leaching out process removes only part of the aluminium and leaves the same crystalline structure. It is therefore postulated that the structure, now unsaturated in so far as aluminium atoms are concerned, is then in a position to form an unstable intermediate/

intermediate compound with hydrogen in which the hydrogen occupies spaces which have been vacated by Aluminium atoms.

This catalyst has been largely used in the work in that, because of its low temperature of preparation, it was extremely active; and since the preparation from the alloy was a relatively simple operation.

It has been applied in a great many catalytic reactions, principally those taking place at low temperature. For example, it has been shown that it is possible to hydrogenate acetone to sec. propyl alcohol at 23°C and 2-3 atmospheres pressure in the liquid phase. (Raney Trans. Am. Chem. Soc. 54, 4116, 1932).

(2) THE STIRRING.

The speed of any chemical reaction which proceeds in stages is dependent upon the slowest step in the chain. Thus in the hydrogenation of a liquid by means of gaseous hydrogen with a solid catalyst, we have the following stages:-

(1) The dissolution of the hydrogen in the liquid

Gaseous hydrogen → Dissolved hydrogen.

(2) The reaction between the hydrogen and the catalyst to form an unstable intermediate.

Dissolved hydrogen + catalyst → Catalyst hydride

(3) The actual hydrogenation reaction

Catalyst hydride + substance → hydrogenated substance + catalyst.

The rate of the combined reaction will largely depend upon the slowest of these single reactions.

It has been shown by Lietz (J. Pract. Chem. 1924, 108, 52.) that in the hydrogenation of sodium cinnamate over nickel, the reaction velocity is proportional to the rate of stirring and independent of the concentration of sodium cinnamate. It is concluded from this that the reaction velocity is determined/

determined by the first two steps above, i.e. by the rate of dissolution of the hydrogen and the time it takes for this dissolved hydrogen to come in contact with the catalyst, and not at all by the third or chemical reaction which must take place very rapidly.

This observation is confirmed by Milligan and Reid (Ind. & Eng. Chem. 1923, 15, 1048) who have shown that the rate of hydrogenation of cottonseed oil over nickel at atmospheric pressure is proportional to the rate of stirring up to 13,000 r.p.m., there being no falling off in this proportionality even at these high rates. It is unfortunate that no one so far has confirmed these results under high pressure.

The stirring of the catalyst in the autoclave has been found to be a most critical point in the work and will be referred to in a later chapter. The maximum speed of stirring was originally 180 r.p.m. but this has been increased in the latter stages of the work to approximately 500 r.p.m. It is pointed out, however, that if the results obtained by Milligan and Reid are valid at high pressures, it may/

may be possible to increase the rate of hydrogenation in the autoclave at least 26 times by a suitable increase in the speed of stirring.

(3) THE TEMPERATURE AT WHICH THE REACTION IS CARRIED OUT.

In general, the speed of a chemical reaction depends upon the temperature, the rate being doubled for every increase of 10 - 15°C. However, in hydrogenation reactions it is usually found that an increase of 50°C is required, and that after reaching a certain temperature, there may be a decrease in the rate. For example, Maxted (J.S.C.I. 1921, 40, 169T.) has shown that the volume of hydrogen absorbed in a given time by 10 ccs of olive oil containing a nickel catalyst varied as follows:-

Temp. of Absorption	80	100	120	140	160	180	200	225	250	°C
Ccs Absorbed	10	78	167	228	238	182	152	88	46	

It will be seen that the temperature of maximum absorption is about 150°C and that from thence up to 250°C there is a marked falling off. It is possible that the reaction would be reversible at high temperatures.

There are several factors that may influence the rate of reaction when the temperature is raised.

(1)/

(1) Hydrogenation reactions are normally exothermic i.e. heat is given out as the reaction proceeds from left to right, an increase in temperature would, therefore, according to the principle of Le Chatelier, tend to alter the equilibrium constant in favour of the reverse reaction.

(2) An unduly high temperature may sinter the catalyst, i.e. the highly extended and porous surface is collapsed and fused at a temperature well below the melting point of the massive metal. The efficiency of the catalyst is thus mechanically reduced.

(3) It has been pointed out, that Lietz has shown that the rate of reaction is mainly dependent upon the dissolution and diffusion of hydrogen. It may be that the effect of increase in temperature is largely due to the increased solubility of hydrogen. If, as Lietz has shown, the actual chemical hydrogenation reaction takes place very rapidly compared to the other stages involved, the rate at which this takes place has little or no effect upon the rate of absorption of hydrogen and no small increase in the activity of the catalyst would have any/

any appreciable effect upon the speed of the combined reaction.

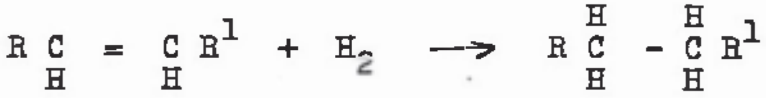
(4) The presence of poisons which may be driven off by an increase in temperature. For example, it is impossible to hydrogenate olive oil below 43°C owing to the accumulation of solid hydrogenation product upon the surface of the catalyst.

In general, Ipatieff (Chem Ztg. 1914, 374.) recommends that platinum and palladium catalysts should be used at temperatures between room and 100°C, nickel between 150 & 200°C, and nickel oxide at 200 - 250°C. Hydrogenolysis normally requires a higher temperature than pure hydrogenation.

In the present work, it has been found that the temperature has been limited by the fact that the compounds to be hydrogenated were very readily decomposed in the presence of the catalyst used.

(4) THE PRESSURE.

Pure hydrogenations are usually accompanied by a decrease in volume



$$R\underset{H}{C} = \underset{H}{C}R^1 + H_2 \longrightarrow R\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}}R^1$$

(liquid) (gas) (liquid)

According to Le Cheteliers principle, increase in pressure would increase the tendency of the reaction to proceed from left to right and the speed of the reaction should be increased by increase of pressure. Armstrong and Hilditch (Proc Roy. Soc. 1921, 100A, 240.) have shown that for cottonseed oil, the rate of reaction is directly proportional to the pressure of hydrogen.

In the reactions under consideration, however, there is no decrease in volume as the reaction proceeds

$$C_2H_6O_2 + 2H_2 \rightarrow C_2H_6 + 2H_2O$$

$$C_2H_6O_2 + H_2 \rightarrow C_2H_5OH + H_2O$$

Indeed, if we assume that the ethylene glycol is always in the liquid phase, there will be an increase in volume unless conditions are such that/

that the water or alcohol formed are condensed out of the system. Increase in pressure will, however, increase the rate of hydrogenation owing to the fact that, under high pressures hydrogen is more soluble in the liquid phase. It has been noted, moreover, that hydrogen at high pressures is in an active, comparable to the nascent, state. (Armstrong T.I.C.E. 1930, 9, 169.

The pressures used have been dictated by the maximum working pressure of the autoclave (3,000 lbs per sq. ins.) and the uncertainties of a high pressure booster pump which was used to fill the autoclave from hydrogen cylinders.

SECTION II.

APPARATUS USED

CHAPTER

V.

THE AUTOCLAVE.

All the high pressure work was performed in a 1,250 ccs. autoclave designed in the College. Full details of this are available in the Industrial Chemist for Dec. 1935 and in a Ph.D. thesis by John F.C. Gartshore, Glasgow, 1936, from which the following short description is taken.

The autoclave and heater assembly are as shown in blue-print No. 1 (in back pocket).

The body and cover plate are forged from billets of Hadfields Hecla 134 which has the following composition:-

Carbon	0.30%
Silicon	0.2%
Sulphur & phosphorus	0.02%
Manganese	0.3%
Chromium	0.4%
Nickel	2.25%
Molybdenum	0.8%
Iron	Remainder

The bottom is hemispherical and is provided with a boss which is pierced so as to provide a means of/

of draining the autoclave. The cover plate is secured by eight equally placed studs, the joint between the autoclave and the cover plate being made by a copper ring in a double spigot. This joint has proved very satisfactory and the joint ring may be used repeatedly provided that it is annealed before each closing.

THE GLAND AND STIRRER.

The form of the gland is as shown in fig. 3. The gland itself consists of alternate gunmetal and leather rings, lubrication being supplied thereto by means of a lantern ring which is fed under balanced pressure from an oil bottle connected to the autoclave. The lubricant flows from the oil bottle to the lantern ring by gravity. The gland is thus oil sealed, any leakage being oil and not gas. The leakage is thereby minimised to a very small amount due to the relatively high viscosity of the lubricant. The gland is tightened by means of a gland nut provided with holes for a tommy-bar. The gland is normally lubricated with glycerol, although it was found that ethylene glycol was/

was equally satisfactory and avoided complications in the analysis of the reaction products.

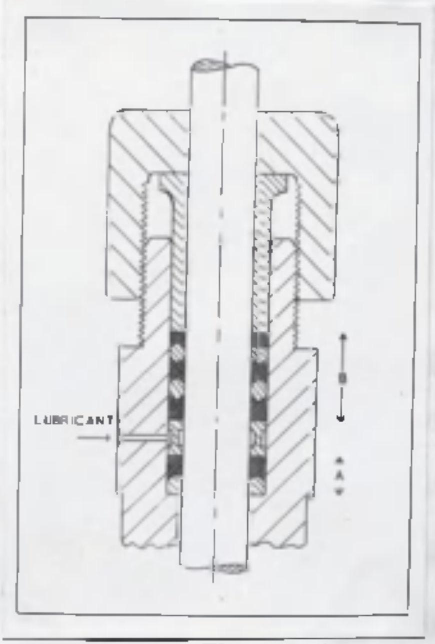


Fig. 3.

The Autoclave Gland.

The stirrer shaft is hollow so as to allow a thermocouple to be passed down to the interior of the autoclave. The upward thrust due to the pressure in the autoclave is taken by means of a Skefco thrust ball-bearing supported on three pillars. The shaft was originally driven by means of a half horse-power motor at a speed of 120 - 180 r.p.m.

HEATING OF THE AUTOCLAVE.

In order to provide a regular and slow rise of temperature, the autoclave body is completely enclosed/

enclosed in a copper block which is heated electrically by a nichrome heater. A clearance of 1/16 of an inch is provided all round between the heater block and the autoclave so that there shall be no local high temperatures. The autoclave is supported within this block on a ring of copper.

TEMPERATURE INDICATORS.

Copper - monel thermocouples are placed

(1) At the foot of the stirrer shaft.

(2) In the copper heating block.

Thermocouples were also at one time welded to the side of the autoclave. These have been removed for reasons which will be discussed later.

CONNECTIONS.

The pipes used for making the connections to the autoclave are of two kinds:

(a) Piping used for cold gases. This is made of mild steel 11/16 inch O.D. by 3/16 inch bore.

(b) That used for hot gases. This is made of a nickel chrome steel (0.8% Ni. 1.1% Cr.) and is also 11/16 inch O.D. by 3/16 inch bore.

(c) Small section pipe for gauge connections etc. This is made of the same steel as (b) and is ¼ inch O.D. by 1/16 bore.

The heavy pipes are much stronger than are required to withstand a pressure of 200 atmospheres, but this size was used on account of the ease with which it is possible to make a lens ring joint with such size of tubing.

PIPE JOINTS.

There are two main classes of pipe joints. That principally used is the I.C.I. lens ring joint fig. 4. The ends of the pipe are coned out at an angle of 20° and the lens ring, which has spherical faces, is fitted between them. The pipe faces are fastened together by four bolts passing through holes in flanges which are screwed to the ends of the pipes. The joint thus formed is a line contact between the spherical surfaces of the lens ring and the coned pipes. This type of joint has proved completely successful, it being possible to make and break the joint repeatedly without damage.

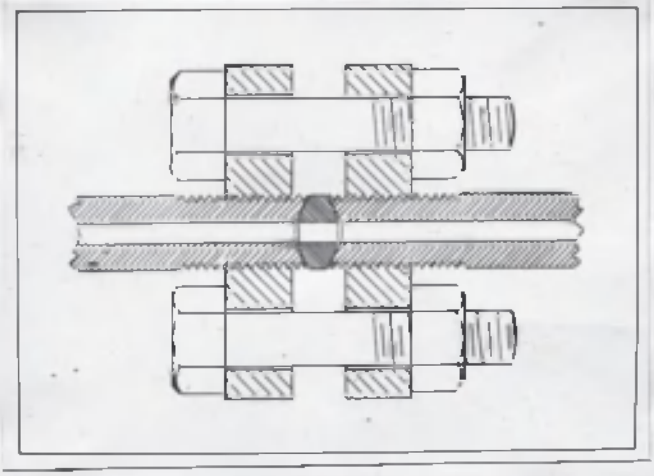


Fig. 4.

I.C.I. Lens Ring Joint.

Unions are used in some places, particularly for gauge connections. The joint is made by means of a copper washer between two V grouved faces. This joint is not so satisfactory, the soldering which is used to make the joint between the pipe and the union being a source of great weakness (fig. 5).

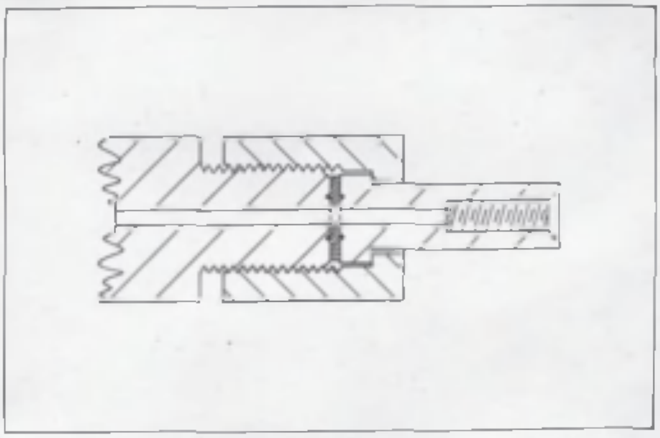


Fig. 5.

High Pressure Union Joint.

VALVES.

These are of three types.

(1) Hopkinson valves. These are intended for use at temperatures up to 500°C. The needle and seat are made of patnam alloy. The needle is loose so that it adjusts itself automatically on its seating. The gland is sealed by means of S.E.A. rings. One of these is fitted as a blow-down valve on the autoclave. It is very rapid in action, it being possible to empty the entire contents of the autoclave in emergency in about five seconds. The inlet and outlet of the valve are tapped and coned for lens ring joints.

(2)/

(2) I.C.I. Valves. These are as shown in fig. 6.

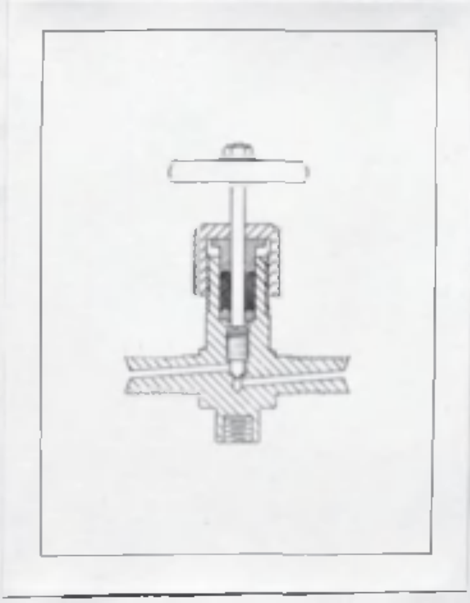


Fig. 6.

I.C.I. Valve.

(3) Budenberg gauge valves. These are made in brass and are used to isolate the gauges in the event of a serious leak occurring.

PRESSURE GAUGES.

These are by Messrs Budenberg, reading up to a maximum of 6,000 lbs. per sq. in. They are enclosed in a steel box and are read by means of a staybright mirror. This safeguards the operator in the event of a burst gauge-tube. Pressure checks are fitted to the gauges to obviate the too rapid application of pressure.

SAFETY PRECAUTIONS.

The entire autoclave is enclosed in a cubicle of removeable 3/16 inch steel sheets and is draughted by means of a Sturtevant fan so that any abnoxious gases may be quickly vented to the atmosphere.

CRITICISM OF THE AUTOCLAVE DESIGN.

During the work done on the autoclave, many defects were noted and some improvements made.

(1) Thermocouple system.

Originally there were three thermocouples welded into slits on the outside of the autoclave body. During an examination of the autoclave, it was noted that the portion around these welds was more corroded than the rest (fig.14). This was thought to be due either to the electrical effect of the two metals forming the couple or to the presence of a channel in the copper block, leading to irregular heating or to the presence of water or both. As the need for these thermocouples in determining temperature gradients was no longer present, they were removed.

(2) Arrangements for blowing down the autoclave.

Originally there was no connection between the blow-down valve and the gasholder. Such a connection was permanently installed so that, in emergency, the contents of the autoclave might be released as soon as possible without dangerous or abnoxious gases being released/

released in the laboratory.

(3) The gland.

As will be seen from fig. 8 the gland is composed of two distinct parts

(a) Two leather washers between the lantern ring and the foot of the gland. These are designed to prevent the lubricant from running into the autoclave.

(b) A series of leather washers and gunmetal rings between the lantern ring and the gland nut follower. This packing serves to prevent the lubricant leaking from the oil bottle to the atmosphere.

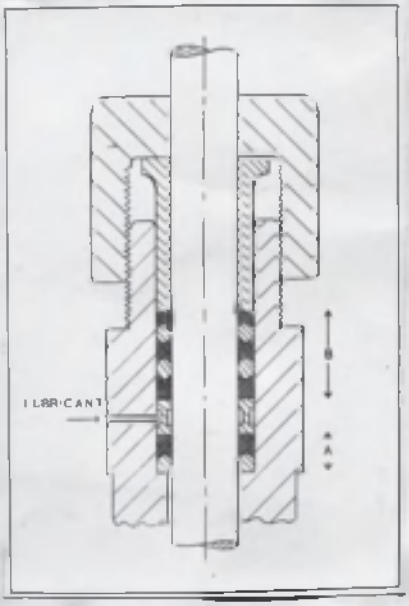


Fig. 8.
The Autoclave Gland.

With well cut leather washers, which were originally cut by hand, it is possible to make the portion of the gland (b) tight even up to pressures of 3,000 lbs. per sq. inch. It could never be guaranteed, however, that lubricant was not leaking down into the autoclave from the oil bottle, even though the pressure difference across that portion of the gland (a) was only of the order of 1 lb. per sq. inch. This leakage was most serious as it led to poisoning of the catalyst when oil was used as a lubricant, and rendered the obtaining of a mass balance impossible when using glycols or glycerol.

The problem of lubricant seeping down the shaft and contaminating the contents of the autoclave is no new one, and many glands have been designed with a view to preventing this. The following is a suggested design by Andreas Hofer (Tongue "Design and Construction of High Pressure Chemical Plant", Chapman and Hall 1934 page 193) which seems to include a number of designs intended to remedy contributary causes. (Fig. 9).

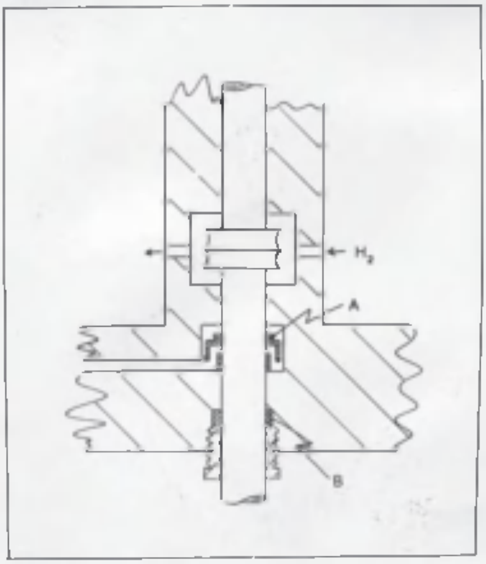


Fig. 9.

Suggested design of a high pressure gland by Andreas Hofer.

(1) To prevent oil seeping down the shaft a special centrifugal separator is placed on the shaft in a chamber from which the oil can be drained (A). The fabrication of this chamber in the cover plate of an autoclave would be a very difficult operation, but even so, no details are given as to how the separator would be fixed or even placed on the shaft, or as to how the shaft would be removed.

(2) For work with substances which would dissolve in the oil and lessen its lubricating qualities, a special fore gland (B) is fitted, while fresh hydrogen entering the autoclave is made to pass/

pass through a special chamber in which the oil soluble vapours mingle with the hydrogen and thus pass back into the autoclave.

Let us examine the reasons why such elaborate schemes for the prevention of oil seeping down the shaft are necessary.

In practice the leather washers used noticeably shrink when in the gland. Thus a gland which is perfectly tight will be found to be quite loose after being left overnight. If considerable shrinkage occurs in the gland during a run and is not immediately taken up by tightening the gland nut, the pressure of lubricant in the lantern ring forces the lower washers of the upper portion of the gland upwards. This leaves the lower portion of the gland loose and allows lubricant to leak from the gland into the autoclave.

If we consider the forces which come into play when tightening down the gland we find that:

Firstly. The coefficient of static friction between leather and smooth steel when lubricated with ethylene glycol is about 0.33. This figure was determined by experiment.

Secondly. The net mechanical efficiency of the/

the gland nut as a machine for tightening down the gland is of the order of 5%, as determined roughly by experiment.

Thirdly. The maximum torque normally employed in tightening the gland nut is about 28 lbs. at 1 foot radius.

Now this torque is capable of producing a total pressure of 2,000 lbs. on the top of the gland. This means that the pressure on the top leathers is about 5,000 lbs. per sq. inch. The leathers themselves are not deformed very far from their natural shape and, being plastic within this range,act as a liquid and transmit the pressure to the containing wall of the gland. This causes a very considerable static frictional force opposing any tendency for the gland to move downwards. Using the figures given above, it has been calculated that the top portion of the gland cannot be moved downwards when the pressure in the lantern ring exceeds 450 lbs. per sq. inch. If therefore we are to prevent the gland lubricant running down the shaft into the autoclave, some provision must be made for tightening the lower portion of the gland. This may be done in either of two ways. First by the division of the gland/

gland into three distinct parts each capable of individual tightening by hand as in fig. (10).

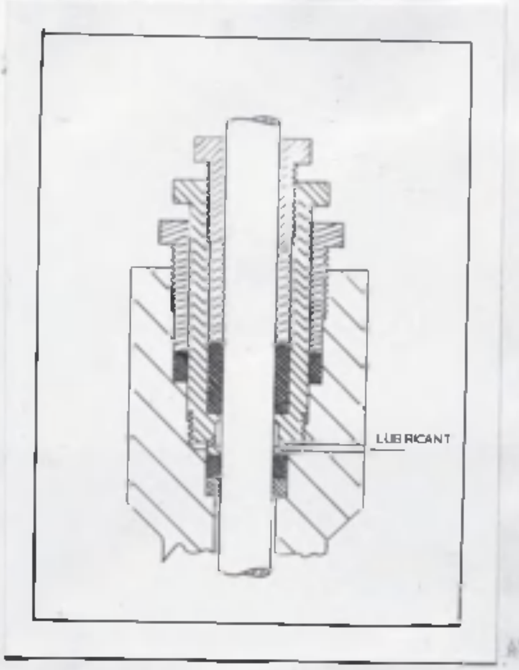


Fig. 10.

Design of a High Pressure Gland.

Secondly, provision may be made for the lower portion of the gland to be self-tightening. This may be done by replacing the lantern ring by a spring which would still keep adequate pressure on the packing despite considerable shrinkage in the gland (fig. 11).

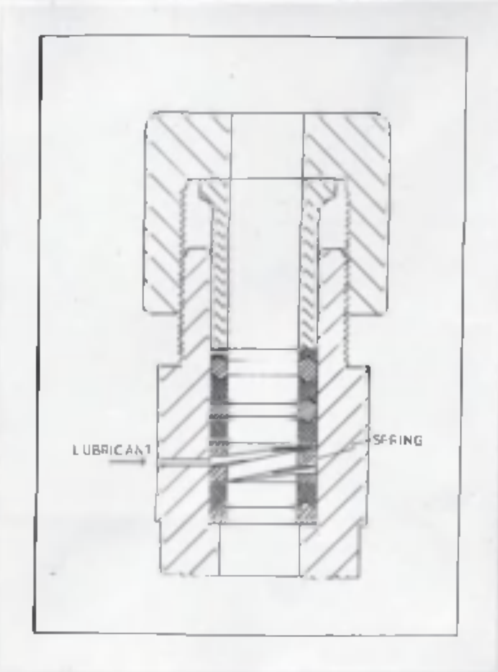


Fig. 11.

Suggested Design of a
High Pressure Gland.

At the same time, it is suggested that leather washers are unsuitable for keeping back the small pressure across the lower portion of the gland, and that a softer material with self-lubricating properties would be more suitable.

This spring was actually designed and made. It was found, however, that by using machine-cut leathers in place of those originally hand cut, and by substituting a Fescolised stirring shaft which enabled the gland to be further tightened, that the leak was greatly minimised.

No further work was therefore done on this aspect of high pressure work owing to lack of time.

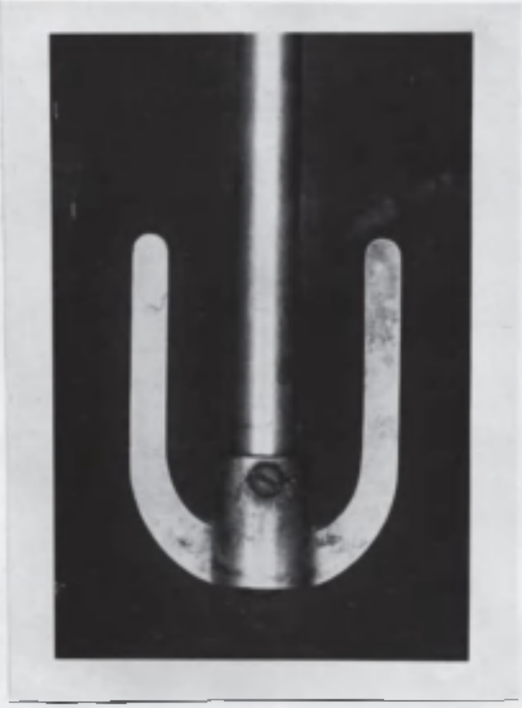
THE STIRRER AND SHAFT.

As will be seen from blueprint No. 1 (in back pocket) the stirrer shaft is supported in two places, at the gland itself, and at the top by the thrust race, the race being carried by three ½" rods. This support is considered to be inadequate considering the very heavy side thrust caused by the driving belt, and in practice the shaft usually runs out of truth, causing excessive wear at the gland.

The fact that autoclave glands have had so much strain placed upon them in the past seems to have led to the adoption of the mixed leather and gunmetal washer variety of gland. Such a gland would undoubtedly be more rigid and would stand a lateral strain much more easily than one composed of leather alone. It is doubtful, however, if such a gland could be usefully employed on a shaft which was properly supported at both ends.

THE STIRRING IN GENERAL.

It has been found (see page 141) that the original design of paddle stirrer, running at 180 r.p.m. was/



Original Paddle Stirrer.

was insufficient to cause intimate mixing of the catalyst, hydrogen, and the substance to be hydrogenated. A chain stirrer was designed and installed (fig. 12). This is working satisfactorily, but it is recommended that provision should be made to stir autoclaves at speeds from 200 to 1,000 r.p.m.

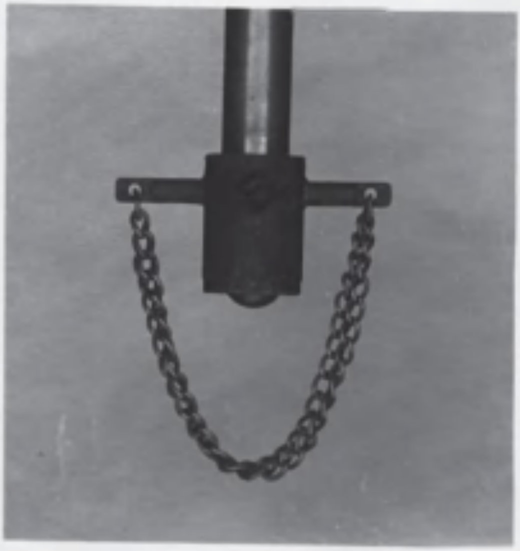


Fig. 12.
Chain Stirrer.

THE OIL BOTTLE.

As has been pointed out, the stirrer shaft usually runs out of truth after it has been in service for a short time. This causes the support for the top of the stirrer to move, carrying with it the oil bottle which is attached to it. There/

There was thus relative motion between the gland pillar which was stationary, and the oil bottle which was being moved by its support. The pipe line between was thereby strained and broke repeatedly. This defect has been remedied by fastening the oil bottle to the wall of the cubicle, and running a pipe line from thence to the gland, so that the oil bottle is now perfectly steady under working conditions. This change has also simplified the manipulation of the autoclave, as the oil bottle does not now require to be removed every time the autoclave is opened. See Fig. (12a)

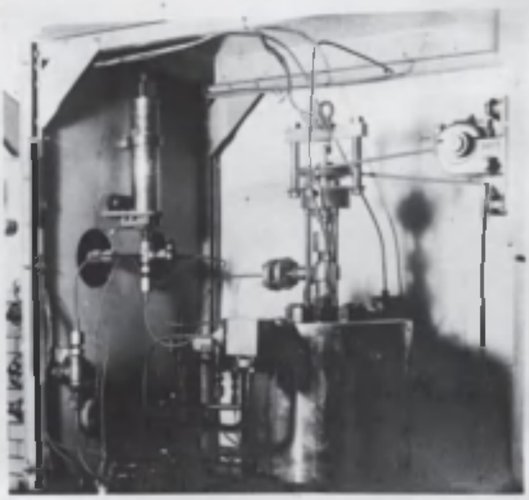


Fig. 12a.

The Oil Bottle Fastened to the Autoclave Cubicle.

THE GAS PASSAGES.

The gas passages leading to and from the autoclave should have been fastened into the body instead of into the lid as at present. This change would obviate the necessity of breaking the joints on the gas inlet and outlet when opening the autoclave.

THE HEATING.

The copper block should be smaller to enable the autoclave to be heated and cooled more rapidly.

It has been shown, for example, that the maximum permissible rate of heating is such as would produce a temperature difference between the outside and inside of the autoclave of 26.6°C (Gartshore Ph.D. Thesis. Glasgow University 1936). The maximum temperature difference that has been noted in practice is of the order of 10°C, and this only at low temperatures. Thus the heating rate may be doubled and still be within the safety factor.

TESTING OF THE AUTOCLAVE.

After the autoclave had been working for approximately 1,000 hours, it was removed from its setting and tested hydraulically to determine, firstly, any increase in size when put under pressure, and secondly, any increase in size due to creep since the last measurements were taken.

The diametral measurements of the autoclave were taken by means of a micrometer, while the vertical measurements were taken by a vernier height gauge from a surface plate. The diametral measurements taken during such a test are shown in the table below:-

Date of Test	Test Pressure	Diameter of Body (inches) 1	11
28: 3: 35	Nil	5.2510	5.2510
	320 atmospheres	5.2526	5.2520
29: 3: 38	Nil	5.2510	5.2509
	320 atmospheres	5.2509	5.2507

Measurements 1 and 11 above are measurements taken at right angles to each other.

It will be seen from this table that there is only a slight (if any) increase in diameter under pressure/

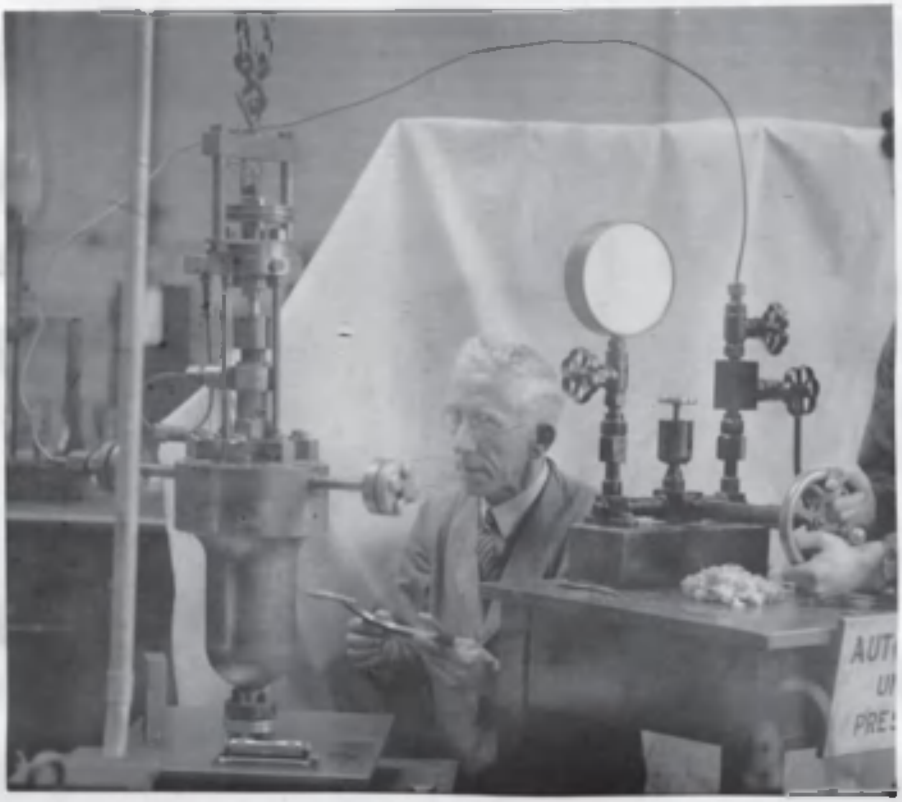


Fig. 13.

Testing the Autoclave.

pressure, and that even after three years use, no detectable growth has taken place. Fig. (13) shows the general layout during the test.

While the autoclave was out of its setting, it was thoroughly cleaned and examined for corrosion. The following details were noted.

(1) The part which had suffered most from corrosion was the underside of the autoclave flange. This was undoubtedly due to the presence at that point of a ring of asbestos sheeting on which the autoclave rested. This asbestos is sufficiently hygroscopic and contains sufficient electrolytes to promote corrosion. The ring of asbestos was therefore removed and replaced by a ring of copper. The corrosion which the autoclave had suffered at this point was, however, unimportant as regards the safety factor.

(2) Copper - monel thermocouples had been welded into slits on the side of the autoclave for the purpose of determining the temperature gradient in the wall. The accompanying photograph Fig.(13a) shows that the corrosion has been more severe at this/

Fig. 14.

The Autoclave showing Corrosion.
29:3:38.

this point. It is not known whether this is due to bad heat treatment after welding, the effect of the dissimilar metals forming the couple, or to the irregular shape of the heater block which was recessed at that point to allow the entry of the thermocouple leads.

In any case, it is not recommended that thermocouples be welded to the sides of autoclaves as they seem to constitute a point of weakness and tend to facilitate corrosion.

OPERATION OF THE AUTOCLAVE.

Normally the gland is lubricated with ethylene glycol or glycerol. Heavy mineral lubricating oils are occasionally recommended for this purpose but it has been found in the College that this is unsuitable for the purpose, the only oils that will lubricate leather being of the fish or vegetable variety. Ethylene glycol, and glycerol, however, are excellent for the purpose and as they were less likely to contaminate the contents of the autoclave, they were used throughout this work.

The leathers themselves should be soaked in ethylene glycol for at least twelve hours before putting in the gland. Too much soaking will cause the leather to swell up unduly and should be avoided as such swollen washers are difficult to fasten in the gland and shrink excessively when the gland is tightened.

The gland should be assembled and tightened about two days before the commencement of the run, the tightening process being repeated from time to time. Such treatment will ensure that the gland will be fairly solid and will not shrink unduly in use.

Normally the solid or liquid to be hydrogenated is introduced into the autoclave in the monel liner, and the copper ring, which should have been previously annealed is pressed in place. The lid, complete with stirrer and gland is then placed in position and bolted down. The nuts, the threads of which are coated with a mixture of white lead and lubricating oil to prevent seizing, are then tightened down in the following order 1,5,3,7,2,6,8,4,

This order is used so that the lid shall be tightened down evenly on its seating.

On connecting up the oil bottle, entrance, and exit tubes, the autoclave is put under a pressure of about 1,000 lbs. per sq. inch with either nitrogen or hydrogen from a cylinder and left overnight. If no large leak is detected by the morning, the gases present in the autoclave are blown down, the current in the heater is switched on, and the steel plates and draught hood are placed in position. The autoclave is then filled to the required pressure with hydrogen and the stirrer set in motion.

On the completion of a run, the autoclave is usually left to cool overnight so that any volatile liquids may condense out and not be present in the gas sample. The gas is then blown down and the autoclave opened.

CHAPTER

VI.

EXAMINATION OF THE PRODUCTS FORMED IN THE AUTOCLAVE.

(a) Gaseous.

The gases were analysed in three types of unit.

(1) The Macfarlane constant pressure gas analysis unit. This is a modified Hempel, the measuring and explosion being done over merdury instead of over water. (Fig. 15).

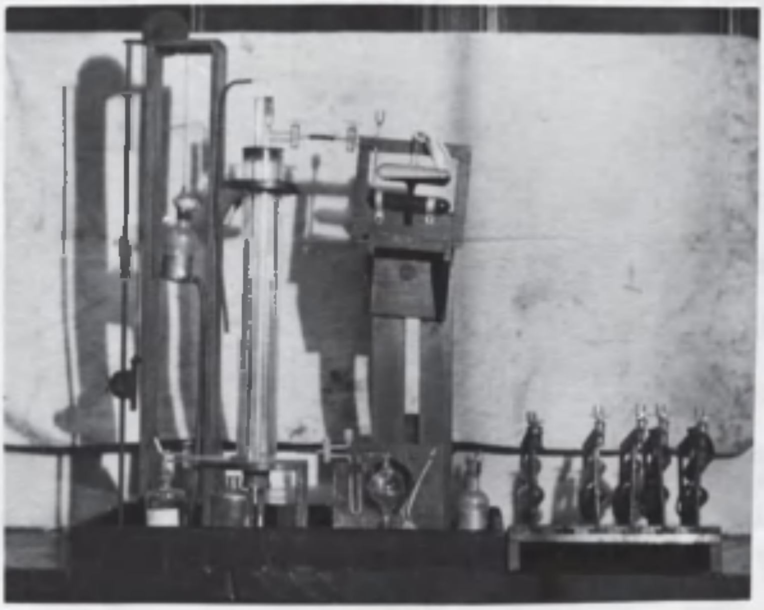


Fig. 15. The Macfarlane Gas Analysis Unit.

Reagents for the absorption of the constituents of the gas are as shown below:-

GAS	REAGENT
Carbon dioxide	25% Caustic potash solution
Oxygen	50% Caustic potash solution + 20% pyrogallol solution
Unsaturated hydrocarbons	Saturated bromine in 10% KBr followed by 10% $Na_2S_2O_3$ in 20% KOH
Carbon monoxide	20% cuprous chloride in conc.HCl + 10% stannous chloride.

The carbon monoxide is absorbed in two pipettes, the first being rejected if the second shows an absorption of more than 1/10 of the first.

The explosion is performed over mercury using a considerable excess of oxygen. After explosion, the gases are led back to the burette and measured to determine the contraction. The carbon dioxide formed by the explosion is then absorbed as before in the caustic potash pipette. A specimen analysis is given below:-

Original volume	50	
$-CO_2$	39.9	CO_2 = 20.2%
$-O_2$	39.6	O_2 = 0.6%
- Unsats	39.6	Unsats Nil
-CO	39.6	CO Nil
Taken for explosion	10.2	
+ Oxygen	50.0	
After explosion	37.2	Contraction 12.8 ;. CH_4=45%
$-CO_2$	31.7	Hydrogen = 9.5%
		Residue - inert 24.7%

(2) A modified Bone and Wheeler unit (Fig. 16)

Fig. 16.

Modified Bone and Wheeler Unit.

In this type of gas analysis unit, the volume of gas present at the end of each absorption is determined by its pressure when expanded to a constant volume at a given temperature. The absorptions are performed by introducing a quantity (5 ccs.) of fresh reagent into the absorption bulb and passing the gas into the bulb on top of the reagent. Intimate contact between the liquid and gas is ensured by rocking the mercury up and down within the bulb. When the absorption is complete, the gas is washed with 5% sulphuric acid solution and its volume again measured. This type of gas analysis unit is more accurate than one of the Hempel variety in that fresh reagents are used each time, thus avoiding contamination with gases from previous analyses which may be dissolved in the reagents.

The reagents normally used in this type of unit are:-

Gas to be absorbed	Reagent
CO_2	33% Caustic potash solution
O_2	Chromous chloride in hydrochloric acid.
Unsaturated Hydrocarbons	Saturated bromine in 10% KBr, the bromine being removed by alkaline pyrogallol.

Hydrogen, carbon monoxide, and saturated hydro-carbons are oxidised in a partial combustion furnace situated at the rear of the apparatus. This makes use of the fact that hydrogen and carbon monoxide may be oxidised over copper oxide at 300°C,whereas a temperature of 900°C is required to oxidise the hydrocarbons present. Thus the presence of heavy hydrocarbons, i.e. hydrocarbons other than methane,may be detected and estimated by the increase in volume during the combustion at 900°C. At high temperatures, however, the copper oxide is apt to give off occluded oxygen. This must be allowed for.

The following gives a specimen analysis:-

Original	947			
-CO$_2$	928	CO$_2$	-	2.1%
-O$_2$	928	O$_2$	-	Nil
-Unsats	923	Unsats	-	0.6%
-H$_2$	738	H$_2$	-	20.0%
-CO	734	CO	-	0.5%
After second combustion	740			
-CO$_2$	43	CH$_4$	-	75.0%
-O$_2$	40	Inert	-	3.8%

(3) A modified Podbielniak apparatus.

This is an apparatus designed to separate gaseous hydrocarbons by fractional distillation. It consists essentially of a boiling bulb, fractionating column and reflux control head as shown on the accompanying diagram (Fig. 17). The boiling of the hydrocarbons is done electrically while the reflux is provided by cooling the top with liquid air.

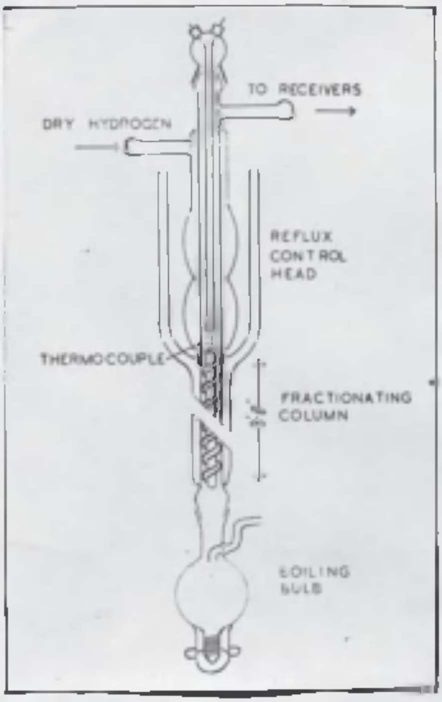


Fig. 17.

Modified Podbielniak Unit.

It is obvious that the cooling required at the top of the column when distilling a high-boiling hydrocarbon is very much less than that required by more volatile hydrocarbons. This variation is provided/

provided for in the reflux control head, which consists of a hydrogen jacket,silvered for half its length, placed between the liquid air and the column itself. This jacket is initially filled with hydrogen which is gradually removed as distillation proceeds from one member of the hydrocarbon series to the next. The heat transferred from the column proper to the liquid air varies as the pressure of hydrogen in the jacket.

The gaseous hydrocarbon, when it leaves the top of the column, passes to the receivers where its volume is measured by its pressure as recorded on mercury manometers. The boiling point of the hydrocarbon is measured by a copper constantan thermocouple placed just below the reflux control head. A graph of thermocouple readings against pressures in the recivers, gives a graph which clearly shows the fractions and their amounts. (Fig. 18).

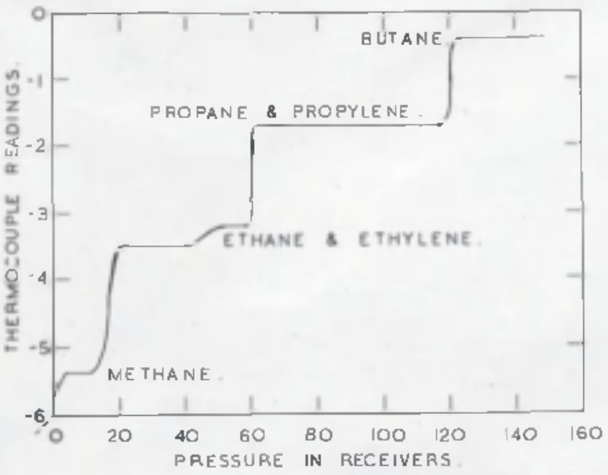


Fig. 18.

Graph of Podbielniak Results.

The column is operated as follows:-

The entire apparatus including the receiver and the hydrogen jacket is evacuated by means of a high vacuum pump. Dry hydrogen is then admitted to the hydrogen jacket to atmospheric pressure and the reflux chamber filled with liquid air. The boiling bulb is also immersed in liquid air.

Meanwhile, the sample to be analysed is freed from carbon dioxide by passage through caustic soda and dried over calcium chloride. The condensible portion is then separated from the permanent gases by passing the sample through a condensing train composed/

composed of two small glass helices with bulbs at the bottom cooled in liquid air. (Fig. 19). These bulbs containing the liquid hydrocarbons are then connected to the boiling bulb by means of the tap provided. The liquid air is then removed from the bulbs and the hydrocarbons distil into the column, where they are again condensed.

Fig. 19.

Condensing Train.

When the sample has thus been introduced into the column, the tap connecting the boiling bulb to the condensing train is closed and distillation is commenced at atmospheric pressure, small amounts of product being taken off to the receivers as the distillation proceeds.

The apparatus was first tested out on a synthetic mixture composed of coal gas, ethylene, and Calor gas; and then with a sample of "200 lb craker gas" from the Scottish Oils Refinery at Grangemouth. The result of the analysis of the latter sample agree favourably with the results obtained with the Podbielniak apparatus in Grangemouth.

The two sets of analyses are compared below:-

Constituent	R.T.C.	Scottish Oils
Methane	6.8%	6.0%
Ethane	13.6%	13.4%
Propane & propylene	43.5%	41.1%
Butane & Higher	21.0%	23.0%

The differences between these two analyses are probably due to inaccuracies in sampling and to the fact that the sample was stored for a considerable time in the College before analysis.

It will be noticed that the propylene and propane/

propane fractions are grouped together. This is due to the fact that their boiling points are so close, that complete separation by fractionation is impossible. In order to end the uncertainty regarding the components of this fraction, a sampling device was installed by which a sample could be obtained from the receivers, each fraction can then be analysed for unsaturated hydrocarbons in the Macfarlane unit.

The figure given for residues in the column when the distillation is finished, given above as butane and higher fractions, is much too large as it embraces one fifth of the total analysis. This is due to the fact that the column is very large and holds up a considerable quantity of liquid which is difficult to remove at the end of the distillation. Various methods have been tried to overcome this difficulty.

(1) The use of a very large sample of about one cubic foot of condensable gases. The proportion of the sample not distilled at the end of the analysis is thereby reduced. This is by far the best method as nothing extraneous is introduced into the column, but/

but it makes the distillation a very lengthy operation.

(2) A known high boiling substance may be introduced into the sample so as to boil the last constituents out of the column. Various liquids have been used for this purpose

(a) Diethyl ether. This was found to solidify out in the column at the low temperatures of distillation and choke the apparatus.

(b) Calor gas, which is a mixture of propane and butane. This operates very well but its use is restricted to the analysis of those mixtures known to contain only methane and ethane. As these mixtures could be adequately analysed on the partial combustion unit, this method was not used after the modified Bone and Wheeler had been installed.

(c) Pentane. This distils very easily through the column, but here again the method is restricted to those mixtures which contain nothing above butane.

EXAMINATION OF PRODUCTS.

(b) Liquid.

It was thought desirable that a fractionating column should be erected for dealing with the liquid products obtained, and that this column should be capable of separating and estimating quantities as small as 5 ccs.

It has been shown by McCabe and Thiele (Ind. Eng. Chem. 1925, 17,605) that the efficiency of such a column in so far as the separation of the liquids is concerned, depends upon two factors, the number of perfect theoretical plates in the column and the reflux ratio. For efficient fractionation the number of perfect theoretical plates must be as large as possible and the ratio of reflux to product should be as high as possible. On the other hand, small quantities of liquid are to be dealt with and the hold-up per perfect theoretical plate should be small. For these reasons, a column of the Dufton type was chosen.

As the column was to function over a fairly/

fairly wide range of temperature, special attention was paid to the method of controlling the reflux ratio. The first column erected has a reflux control head similar to that used in the modified Podbielniak apparatus (Page 68). The hydrogen jacket was replaced by a jacket containing mercury. The height of the mercury was adjusted according to the cooling required to maintain an adequate reflux ratio. The mercury was cooled by means of a water jacket. Any vapour which escaped condensation by this "dephlegmator" was condensed by the condenser alongside and was taken as product (Fig. 20).

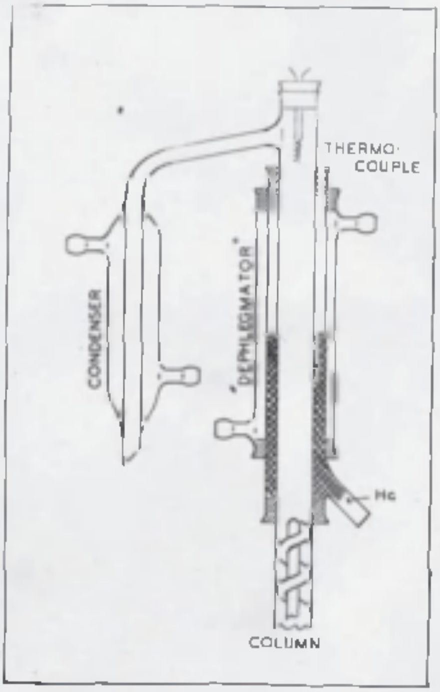


Fig. 20.

Fractionating Column.

Fractionating Column.

The column was lagged with asbestos wool. With this, however, it was found impossible to fractionate anything boiling above 100°C owing to condensation in the column. A second fractionation apparatus was therefore designed embodying certain improvements suggested by the failings of the first column.

This second apparatus had two main differences from the first.

(1) The reflux was controlled in a much more simple and certain manner. In the first column the amount of reflux sent back down the column was fixed by the height of mercury in the jacket. Any unevenness in the boiling rate due to bumping, draughts, etc., would therefore have a considerable effect upon the product rate since it is so small compared with the reflux and boiling rates. The reflux ratio would therefore alter considerably.

The height of the mercury in the jacket had, moreover, to be altered as distillation proceeded from one component to the next in order to keep the reflux ratio even approximately constant. These two defects/

defects were remedied by fixing the product rate. In this system all the vapours ascending the column are condensed and returned except a small portion which could be steadily withdrawn by means of a tap provided (Fig. 21).

(2) Heat loss from the column was prevented by surrounding it with an electric heater.

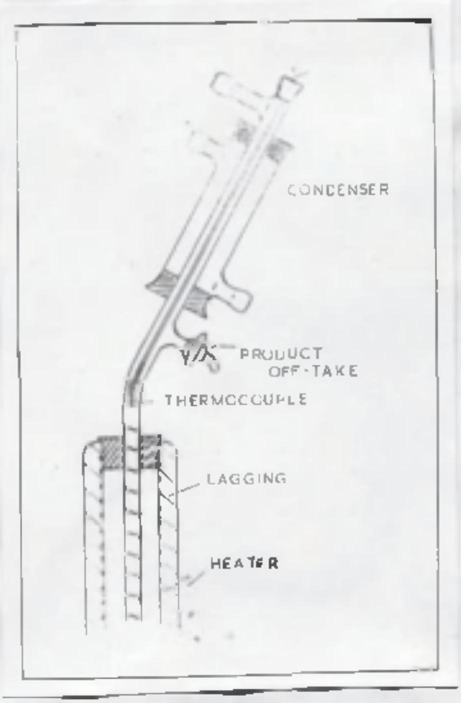


Fig. 21.

Fractionating Column
-2-

The column worked perfectly as regards the control of the reflux ratio was concerned. The heater, however, was not so satisfactory as it tended to overheat the column. Thus when fractionating/

fractionating a mixture of ethylene glycol and water, it was necessary to heat up the whole column to a temperature of 200°C in order to prevent the glycol condensing completely before it reached the condenser proper. This superheated the water in the upper part of the column and prevented any whatsoever descending, usually resulting in the fracture of the column. A third apparatus was therefore designed in which heat loss from the column was prevented by means of a vacuum jacket. This column has proved very satisfactory and is shown in fig.(22).

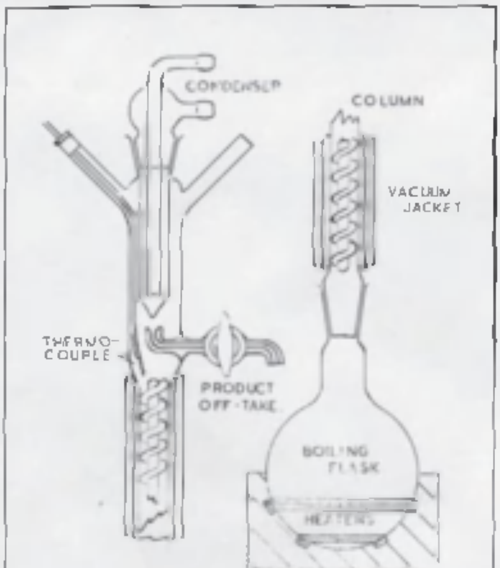


Fig. 22.

Fractionating column.
-3-

Fig. 22.

Fractionating column -3-.

General view.

The packing is composed of a 3/16 inch glass rod surrounded by a 1/10 inch aluminium wire, four turns being to the inch. This packing is a tight fit inside a 3/8 inch glass tube which serves as the column proper. The liquid to be fractionated is contained in a round-bottomed flask which is heated electrically by means of two coils of nichrome wire of resistance 45 and 85 ohms respectively. These resistance coils are let into slots carved in a diatomaceous brick which supports the flask, and are arranged so that they may be used individually or in series, the current in them being controlled by an ammeter and resistance. This method of heating was chosen because it can be instantly varied, there being very little time lag, as most of the heat is supplied to the flask as radiant heat, while the diatomaceous brick remains comparatively cool.

The vapours, after ascending the column , are condensed by means of an inner tube condenser arranged so that the liquid drops into a small cup (Fig. 23). From this cup,the product is withdrawn from the column at a steady rate while the remainder overflows back down as reflux. The reflux ratio used/

used may be determined roughly by counting the number of drops from the condenser and tap respectively.

Fig. 23.

Fractionating column -3-.

View of top of the column.

SECTION III

EXPERIMENTAL.

CHAPTER

VII.

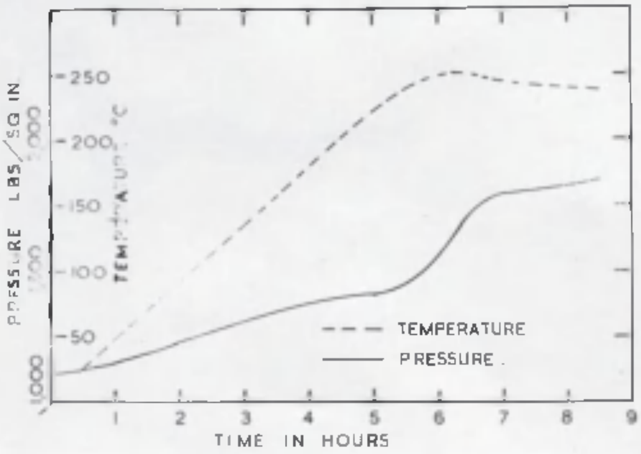


Fig. 24.

Autoclave conditions during
hydrogenation of ethylene glycol.

PRELIMINARY WORK ON THE HYDROGENATION OF GLYCOLS.

The first step in the work was to repeat those experiments which had been done in the College by Mr. J. Angus (see page 12).

The autoclave was therefore charged with the following in an attempt to hydrogenate ethylene glycol.

120 ccs. Ethylene glycol.

Hydrogen to 1100 lbs per sq. inch.

Raney nickel (prepared some time previously and stored under alcohol)..........1.7 gms.

The lubricant used in the gland was ethylene glycol and the charge was stirred during the course of the reaction with the paddle stirrer in the normal position.

The course of the reaction followed closely that which previous work had indicated, the notable point being the rise in pressure when the autoclave had reached a temperature of 255°C (see Fig. 24).

The products of this reaction were,

Blow-down/

Blow-down gas. approximately 73 litres of a gas of the following composition:-

Carbon dioxide	10.4%
Hydrogen	30.0%
Methane	47,6% (No ethane being detected in a Podbielniak analysis)

LIQUID LEFT IN THE AUTOCLAVE. This consisted of

Methyl and ethyl alcohol...	5.5 gms.
Water, containing a trace of formic acid	29 gms.
Residue of unchanged ethylene glycol.	

No mechanism for this reaction was then known, although it was suspected that the glycol was being hydrogenated to methyl alcohol, and that this reaction was followed by decomposition of the alcohol to carbon monoxide and hydrogen.

$$C_2H_4(OH)_2 + H_2 \longrightarrow 2CH_3OH + H_2O$$

$$CH_3OH \longrightarrow CO + 2H_2$$

It/

It was considered possible, however, that some of the products had been formed by the thermal decomposition of the glycol, and an investigation was made into the products obtainable by heating ethylene glycol alone to a temperature of 300°C in the autoclave.

In this experiment, a small rise in pressure was noted when the temperature had reached 250°C, and when cold, the autoclave contained

Gas (about 4 litres) consisting of

CO_2	12%
Unsats	2.4%
CO	15.4%
CH_4	13.2%
H_2	29.0%

Residue inert (probably N_2 from testing)

LIQUIDS.

The liquid part of the product contained Methyl alcohol (1.3 ccs.),water, and ethylene glycol.

It/

It will be seen that all the products of the so-called hydrogenation appear as products in the pyrolysis experiment where no hydrogen was originally present. This led to the belief that the main reaction was the catalytic decomposition of the glycol, followed by the hydrogenation of the products of the first reaction. In this case the experiment would have little interest as a hydrogenation. According to Nef (Ann. 1904, 335, 200) ethylene glycol can be passed over pumice at a temperature of 500°C at atmospheric pressure without decomposition, so that, at the time, it was considered that pyrolysis of the glycol in the hydrogenation experiment was unlikely, owing to the low temperature, and the considerable hydrogen pressure used.

In order to prove that this decomposition was actually being catalysed by the Raney nickel, ethylene glycol was heated with the catalyst alone in the autoclave to a temperature of 255°C.

The results of this and the two previous experiments are tabulated below for comparison:-

	"Hydrogenation"	Pyrolysis 1	Pyrolysis 11
Charge in the autoclave			
Ethylene glycol	120 ccs.	100 ccs.	100 ccs.
Hydrogen	95 litres (8.8 gms.)	Nil	Nil
Raney Nickel	1.7 gms.	Nil	2.5 gms.
Analysis of gas formed	73 litres	4 litres	37 litres
CO_2	10.4%	12.0%	33.0%
H_2	30.0%	29.0%	--
CH_4	47.6%	13.2	53.5%
Unsats	--	2.4%	--
CO	--	15.4%	--
Analysis of liquid products			
Methyl alcohol	5.5 ccs.	1.5 ccs.	1.8 ccs.
Water	29 ccs.	--	6 ccs.

It will be seen that there is substantially no difference between the experiment performed with, and those performed without hydrogen being present, except that the quantity of methyl alcohol formed is greater in the case of the hydrogenation, presumably because of the greater pressure which is used in this experiment. It is also to be noted that, when the catalyst is present, there is a marked increase in the volume of decomposition products, and that carbon monoxide is no longer present at the end of the reaction/

reaction, due, presumably, to its having been hydrogenated to methane.

The pyrolysis of hydroxy compounds was further studied in that it might afford an insight into the hydrogenation of sugars and show in how far the results of previous workers are due to pyrolysis alone or to hydrogenation in addition to pyrolysis.

CHAPTER

VIII.

THE PYROLYSIS OF GLYCOLS.

The pyrolysis of ethylene glycol was first accomplished by Nef (Ann. 1904, 335, 200) who showed that it was possible to decompose ethylene glycol over pumice at 550°C. From 40 gms. of starting material there was obtained:-

7 ccs. acetaldehyde.
5 ccs. water, together with traces of crotonaldehyde
14.4 ccs. unchanged ethylene glycol.

The gaseous product amounted to 4.5 litres and consisted of

CO	50.0%
H_2	11.5%
CH_4	38.5%

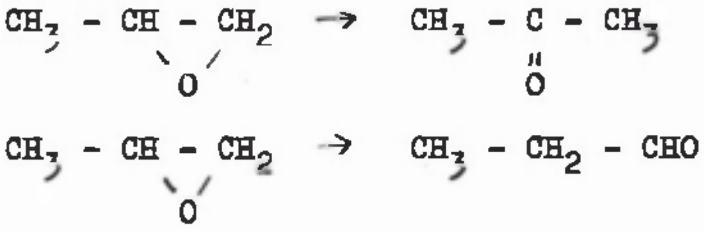
The mechanism suggested for this reaction was the major decomposition of the glycol to acetaldehyde and water, involving dehydration and tautomeric changes

$$CH_2OH\text{-}CH_2OH \quad = \quad CH_3\text{-}CHO + H_2O$$

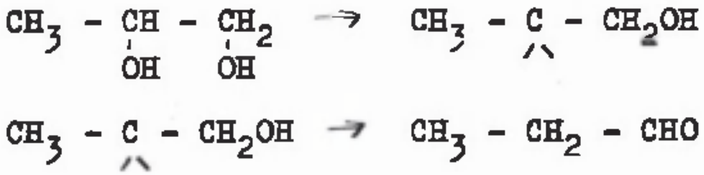
and/

and the subsequent pyrolysis of acetaldehyde to give methane and carbon monoxide.

Nef also pyrolysed 1.2, propylene glycol over pumice at 500°C. Propionaldehyde was the major product of this reaction. Acetone was not reported as a product and it was thus assumed that the reaction could not proceed through the intermediate propylene oxide stage, since propylene oxide decomposes to give propionaldehyde and acetone in the ratio of two mols propionaldehyde to one of acetone



Nef suggested that the mechanism of the reaction is as follows:-



$$CH_3-\underset{OH}{CH}-\underset{OH}{CH_2} \rightarrow CH_3-\underset{\wedge}{C}-CH_2OH$$

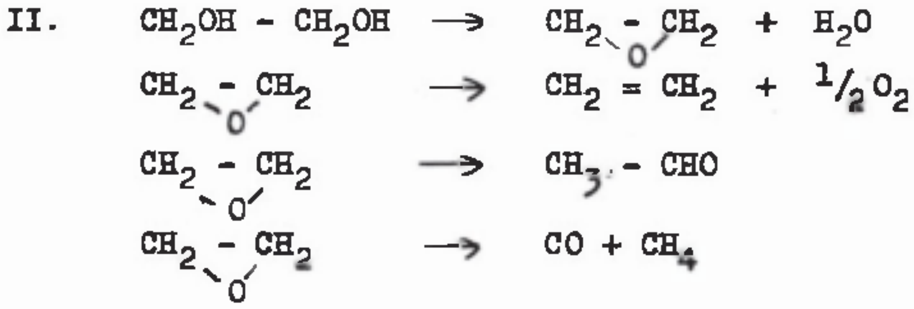
$$CH_3-\underset{\wedge}{C}-CH_2OH \rightarrow CH_3-CH_2-CHO$$

This involves dehydration to a bivalent carbon atom and rearrangement of the molecule.

Drake and Smith (J. Am. Chem. Soc. 52, 4558, 1930) examined the decomposition of ethylene glycol over a vanadium pentoxide catalyst. Acetaldehyde and ethylene were the main products of the reaction. The mechanism of the reaction suggested was:-

I. $CH_2OH - CH_2OH \rightarrow CH_2 = CHOH + H_2O$

$CH_2 = CHOH \rightarrow CH_3 - CHO$



II. $CH_2OH - CH_2OH \rightarrow CH_2 \underset{O}{-} CH_2 + H_2O$

$CH_2 \underset{O}{-} CH_2 \rightarrow CH_2 = CH_2 + {}^1/_2 O_2$

$CH_2 \underset{O}{-} CH_2 \rightarrow CH_3 - CHO$

$CH_2 \underset{O}{-} CH_2 \rightarrow CO + CH_4$

III. $CH_2OH - CH_2OH \rightarrow CHO - CHO + 2H_2$

$CHO - CHO \rightarrow 2CO + H_2$

Ipatieff (J. Russ. Phys. Chem. Soc. 35, 542, 1903; 36, 3892) compared the dehydration of glycols in a copper tube filled with alumina with the decomposition under high pressure in an autoclave. The same results were obtained in each case. Complete decomposition/

decomposition of the glycol occurred in one hour at 400°C under pressure. The liquid products consisted of acetaldehyde and water with small proportions of paraldehyde and crotonaldehyde. The mechanism suggested was the initial production of ethylene oxide which isomerises to the aldehyde. The latter partly polymerises to the paraldehyde, while crotonaldehyde is produced by an aldol condensation. This work of Ipatieff's has been largely confirmed by Sabatier.

Trillat (Bull. Soc. Chim. 3, 29, 35, 1903.) passed the vapour of ethylene glycol over a platinum spiral at 90°C and noted that the spiral was raised to incandescence yielding formaldehyde, glyoxal, and glycollic aldehyde.

Pyrolysis of the higher glycols has been studied by Kyriakides (J. A. C. S. 36, 980, 1914) who has shown that phenyl and diphenyl ethylene glycols may be decomposed at 250 - 300°C to give the corresponding aldehydes

$$C_6H_5CHOH - CH_2OH \rightarrow C_6H_5CH_2 - CHO + H_2O$$

$$(C_6H_5)_2COH - CH_2OH \rightarrow (C_6H_5)_2CH - CHO + H_2O$$

whereas/

whereas at 400 - 450°C the same glycols give ketones exclusively

$$C_6H_5CHOH - CH_2OH \rightarrow C_6H_5CO - CH_3 + H_2O$$

Hydrobenzoin also decomposes at 400 - 450°C to give phenyl benzyl ketone

$$C_6H_5 - CHOH - CHOH - C_6H_5 \rightarrow C_6H_5 - CH_2 - CO - C_6H_5;$$

benzaldehyde is also produced as a by-product. It is noteworthy that in none of the above experiments on the pyrolysis of the higher glycols is an ethylene oxide compound formed.

This review of the literature can be summarised as follows:-

(1) In the absence of catalysts, decomposition proceeds almost entirely to the aldehyde or ketone stage. This may further decompose.

(2) In the presence of catalysts, the above no longer holds and the reaction proceeds upon an entirely different and uncertain path.

The experimental work on this subject

has/

has proceeded along three main lines

Pyrolysis over pumice.

Pyrolysis over nickel in the vapour phase.

Pyrolysis over nickel in the liquid phase.

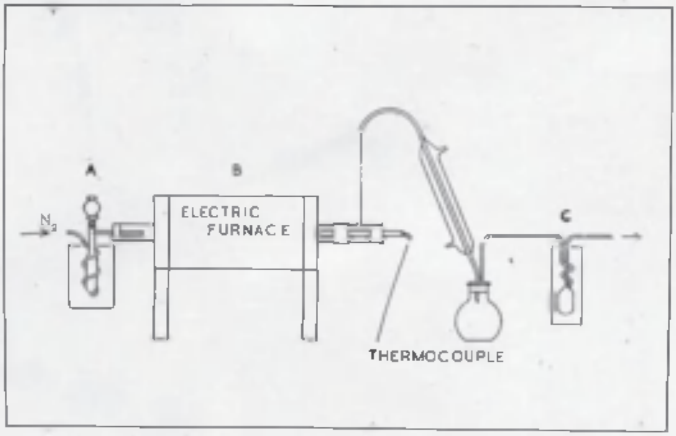


Fig. 24a.

Apparatus used for the pyrolysis of glycols.

DECOMPOSITION OF GLYCOLS. (1) Ethylene glycol.

(a) Vapour phase pyrolysis (atmospheric pressure).

The apparatus in which these experiments was performed is shown in fig. (24a). In this the glycol was vapourised in a stream of nitrogen and passed over pumice which was heated to the required temperature in an electric furnace. The liquid products of the reaction were removed by a condensing train and the gas was collected in aspirators.

The nitrogen used for the vapourisation was found to contain some 1% oxygen, it was therefore purified by passing through alkaline pyrogallol solution. The nitrogen was then passed through the vapouriser (A) which was maintained at a temperature of 300°C where the glycol was vapourised and entered the gas stream. This nitrogen and glycol vapour then passed to the reaction tube (B) which was made of silica 2.4 cms. diameter with a heated length of 50 cms. After passage through the tube, the gas is cooled first with water and then by means of a condenser immersed in solid CO_2 in ether (C). A wash bottle containing magnesium sulphate serves to/

to scrub the gas before it passes to the aspirators.

In an experiment upon the pyrolysis of ethylene glycol over pumice at 550°C the following was obtained:-

GAS

CO_2............	8.6%	Total 0.63 gms.
Unsats.........	8.6%	
CO.............	35.2%	
CH_4............	32.5%	
H_2.............	14.9%	

Residue inert.

LIQUIDS

Water..........	0.43 gms.
Acetaldehyde...	0.1 gms.
Unknown ester..	0.14 gms.

The rate of flow of the glycol over the pumice was 0.036 gms. per minute and 33% of the glycol decomposed per pass over the pumice.

This/

This result confirms the work of Nef and Ipatieff in that acetaldehyde is a product of the decomposition.

Under similar conditions it is found that acetaldehyde decomposes to give a gas composed of

CO_2	6.5%
Unsats	4.1%
CO	36.7%
CH_4	29.8%
H_2	9.0%

There are no liquid products.

This gas shows a marked similarity to that obtained in the pyrolysis of ethylene glycol over pumice, and thus confirms the observations of Nef who postulated acetaldehyde as an intermediate product in the decomposition of the glycol.

In view of the fact that the decomposition of ethylene glycol was so markedly accelerated by the presence of nickel in the high pressure reactions, a nickel on pumice catalysts was prepared in order that/

that the decomposition over this metal might be studied. The same apparatus was used as in those experiments without catalyst, the pumice being replaced by a nickel on pumice catalyst.

The catalyst was prepared as follows:-

A solution of nickel nitrate was prepared by dissolving 39.06 grams of the hexa-hydrate in water. This was added to 100 gms. of acid washed pumice and the whole was evaporated to dryness in a basin and heated at about 500°C to the oxide in a Battersea crucible. This oxide was then charged into the silica tube and the apparatus assembled. The air was then swept therefrom by means of a stream of nitrogen and the oxide reduced by heating in a stream of hydrogen for six hours at 350°C. This reduced catalyst was kept in an atmosphere of hydrogen or nitrogen to prevent oxidation.

Using this catalyst it was found that the ethylene glycol decomposed completely to gas and water at 350°C.

The gaseous products were:-

CO_2	7.1%
Unsats	0.4%
CO	24.6%
CH_4	24.9%
H_2	38.4%

The rate of decomposition was 0.02 gms. per minute.

It was realised, however, that the nickel in this highly active form would catalyse not only the decomposition of the glycol, but also the following well-known gas reactions:-

(1) $CO + H_2O = CO_2 + H_2$

(2) $CO + 3H_2 = CH_4 + H_2O$

As it was desired, if possible, to determine the primary products of decomposition, an effort was made to deactivate the nickel in so far as these gas reactions were concerned. This was successfully accomplished by oxidising the catalyst at 800°C for 1-2 hours and reducing again with hydrogen for 4 hours/

hours at 400°C.

It was found that although the activity of this de-activated catalyst, in so far as pyrolysis was concerned was unaltered, the percentage of methane and carbon dioxide present in the products of decomposition was largely reduced. The table below gives the products of decomposition of ethylene glycol using both the normal and de-activated catalyst.

	Using normal catalyst.	Using de-activated catalyst
Temperature	350°C	300°C
Gas analysis (Nitrogen free basis)		
CO_2	11.0%	2.0%
Unsats	0.2%	0.6%
CO	29.8%	40.0%
CH_4	22.7%	1.9%
H_2	38.3%	54.5%

The decomposition over the catalyst cannot therefore take place through the intermediate aldehyde stage as this would decompose to give a gas composed almost exclusively of methane and carbon monoxide.

As/

As will be seen above, when the nickel is deactivated in so far as the gas reactions are concerned, very little methane is formed.

(b) Liquid phase pyrolysis (atmospheric pressure).

In order to determine accurately the primary products of the decomposition, the pyrolysis of the glycol was conducted in such a way that any products formed were immediately removed from the presence of the catalyst, in a stream of glycol vapour. The glycol is then removed by a condenser maintained at 100°C while the products are carried over to a second condenser where they are removed. Any gas formed is collected and analysed.

It is assumed that any products of the decomposition are liquid and boil below the boiling point of ethylene glycol. This will be so unless there is association of two or more molecules of ethylene glycol, and as such were not found in the work in the autoclave under high pressure, it was not anticipated that they would be formed under atmospheric pressure at 200°C.

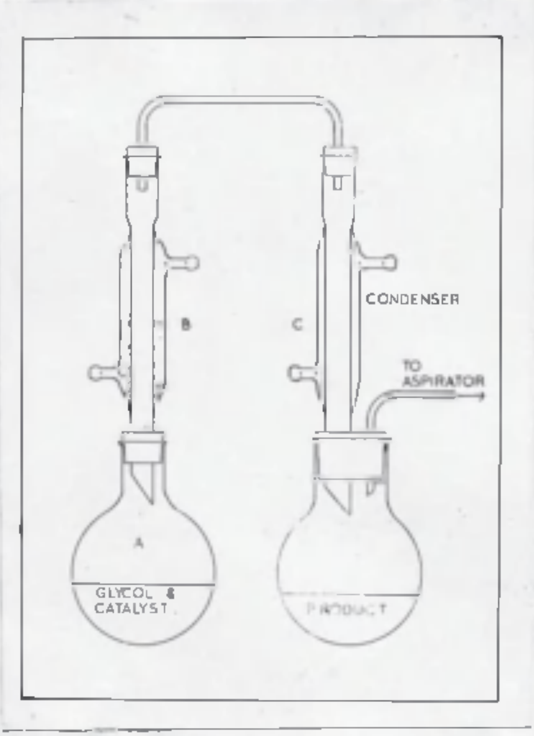


Fig. 25.

Apparatus used for the liquid phase pyrolysis of ethylene glycol.

The apparatus is as shown in fig. (25) and consists of

(A) A 500 ccs. flask in which the glycol and catalyst are boiled.

(B) A reflux condenser maintained at 100°C by means of boiling water therein, and which is designed to return the ethylene glycol to the flask.

(C) A condensing train and aspirator in which the products of decomposition are collected.

The catalyst used for this work was Raney nickel, as this was the most active obtainable. The decomposition was very slow, however, as the boiling point of ethylene glycol is well below the temperature at which decomposition proceeds in the absence of a catalyst (550°C) or in the presence of nickel on pumice (300°C).

In three hours 0.125 cu.ft. of gas were collected together with 3.5 ccs. of a liquid which proved to be mainly water together with a trace of an identified aldehyde, which was not, however, acetaldehyde.

The/

The gas consisted of:-

CO_2	2.8%
Unsats	0.8%
CO	20.8%
CH_4	16.6%
H_2	58.4%

This experiment confirms the view previously advanced that acetaldehyde is not the principal primary product of the reaction since any acetaldehyde formed would have been swept over into the condensers where it could easily have been identified and the yield of gas would have been small compared with the yield of liquid products.

The hydrogen content of the gas is so high that it would seem that it and the unidentified aldehyde, which may be glyoxal, are the products of one of the primary reactions. This confirms the view advanced by Drake and Smith (J.A. C. S. 52, 4558, 1930) who suggested that the mechanism of the decomposition is

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CHO \\ | \\ CHO \end{array} + 2H_2$$

On/

On the other hand, if this were the only reaction taking place, there would be no carbon monoxide or methane formed, in the liquid phase pyrolysis since it is impossible to visualise the glycollic aldehyde decomposing at 200°C in the absence of a catalyst. There must be then another reaction taking place in which the glycol decomposes completely to gas without any intermediate stage.

In this it is to be noted that in these experiments the Raney nickel is acting as a dehydrogenating catalyst (Comptes Rendus 1939, 208, 109 - 112) and that in the autoclave under pressure of hydrogen, the reaction would probably become a balanced reaction. The possibility of hydrogenating an intermediate product of the decomposition is therefore not worth further consideration.

PYROLYSIS OF 1:2 PROPYLENE GLYCOL.

(1) High pressure.

In the autoclave in the presence of Raney nickel and at a temperature of 280°C, 1:2 propylene glycol decomposes in much the same way as ethylene glycol. For this experiment the charge in the autoclave was

100 ccs.	Propylene glycol
8 gms.	Raney nickel.

A rise in pressure was noted at a temperature of 235°C. The products of the reaction were:-

GAS (about 37 litres):-

CO_2	22.6%
Unsats.	1.0%
CH_4	70.6%

Residue inert.

LIQUID

Acetone	0.66 ccs.
Water	6.5 ccs.
Unchanged glycol	17 ccs.

(2) Decomposition at atmospheric pressure.

Under atmospheric pressure, propylene glycol decomposed as follows:-

	Over Pumice.	Over Ni on pumice.	Over de-activated Ni on pumice.
Temperature	550°C	300°C	300°C
Products.			
Gas	0.98 gms.	3.19 gms.	1.95 gms.
CO_2	7.3%	1.9%	1.2%
Unsats.	13.6%	0.7%	1.8%
CO	35.5%	37.6%	39.1%
CH_4	38.2%	25.6%	23.0%
H_2	Nil.	32.8%	34.6%
Liquids			
Propionaldehyde	0.23 gms.	--	--
Water	2.1 gms.	--	--
Acetone	Trace	0.65 gms.	0.223 gms.
Rate of decomposition	0.029 gms/min.	0.05 gms./min.	0.027 gms./min.
Percentage decomposition	70.7%	46.8%	59.1%

It/

It will be noted that the percentage of methane does not alter appreciably when the catalyst is de-activated. This leads us to suppose that the bulk of methane formed is due to pyrolysis and not to the hydrogenation of carbon monoxide.

It would seem from the results shown above that the main primary decomposition is to acetone and water.

Under similar conditions, however, an equimolecular mixture of acetone and water decomposed as follows:

	Over Pumice	Over Ni on Pumice.	Over de-activated Ni on pumice
Temperature	550°C	300°C	300°C
Gaseous products			
CO_2	1.3%	5.3%	19.4%
Unsats.	16.8%	19.2%	1.5%
CO	43.9%	35.7%	12.0%
CH_4	31.6%	36.5%	39.0%
H_2	--	--	21.0%
Liquid products			
Acetic acid	Trace	Trace	Not detected
Percentage decomposed	27.7%	15.5%	7.9%
Rate of decomposition	0.013 gms/min.	0.019 gms/min.	0.004 gms/min.

This table shows that the decomposition of acetone is harder to accomplish than the decomposition of 2, 3, propylene glycol. For example, the percentage of acetone decomposed over de-activated nickel on pumice is only 7.9%, the rate of decomposition being 0.004 gms/min; whereas under similar conditions the percentage of 1,2, propylene glycol decomposed is 59% with a decomposition rate which is 7 times as great. It would therefore seem impossible for acetone to be the main intermediate product in the decomposition.

Although no further work has been done on the decomposition of this glycol, it is assumed that in this case also, the primary reaction in the presence of catalysts is the loss of hydrogen with the formation of a glyoxal derivative or the complete disruption of the molecule.

PYROLYSIS OF 2:3 BUTYLENE GLYCOL.

(1) At high pressure.

In the autoclave in the presence of Raney nickel; 2,3, butylene glycol decomposed to give methyl ethyl ketone and water at 260°C. The yield of the ketone was high, being about 60%, and only a very small quantity of gas was formed, 20 litres being obtained from 200 ccs. of the glycol.

The gas consisted of:-

CO_2	25.0%
Unsats	0.2%
CO	0.2%
CH_4	70.0%
C_2H_6	2.5%

In this case it is obvious that the major decomposition product is to methyl ethyl ketone and water. It is assumed that the gas came from the decomposition of a small portion of the methyl ethyl ketone.

(2) At atmospheric pressure.

At atmospheric pressure the decomposition proceeded on very similar lines, methyl ethyl ketone and water being the main products, together with some gaseous products of the decomposition of the ketone.

The table below gives the results obtained

	Over Pumice	Over Ni on Pumice	Over Ni on Pumice (deactivated)
Temperature	550°C	300°C	300°C
Gas formed	0.7 gms.	0.52 gms.	0.786
CO_2	3.3%	12.9%	3.0%
Unsats.	14.9%	0.9%	0.4%
Ch_4	29.8%	39.7%	27.5%
CO	20.7%	19.8%	26.1%
H_2	20.7%	23.3%	37.3%
Percentage decomposition	74.4%	63.9%	50.7%
Decomposition rate	0.046 gms/min.	0.007 gms/min.	0.035gms/min.
Liquids formed	3.1 gms.	0.123 gms.	1.12 gms.
Methyl ethyl ketone	1.9 gms.	0.123 gms.	1.12 gms.
Water	1.2 gms.	--	--

CONCLUSIONS WITH REGARD TO THE WORK ON THE PYROLYSIS OF GLYCOLS.

The previous work which has been done, together with the work that has been done in the College, has led to the formulation of the following general rules:

(1) In the absence of catalysts, glycols having their hydroxyl groups on two adjacent carbon atoms decompose at temperatures of about 550°C by losing water with the subsequent formation of an aldehyde or ketone. This aldehyde or ketone may further decompose.

(2) In the presence of catalysts, particularly of the nickel type, glycols having their hydroxyl groups on adjacent carbon atoms at the end of the chain, decompose by losing hydrogen with the formation of a glyoxal derivative or the complete disruption of the molecule.

(3)/

(3) Glycols having hydroxyl groups on adjacent carbon atoms which are not at the end of a chain, decompose with the loss of water to give ketones both with and without a catalyst being present.

CHAPTER

IX

THE HYDROGENATION OF GLYCOLS ABOVE THEIR DECOMPOSITION TEMPERATURE.

This investigation was carried out to see in how far the hydrogenation of the glycols could be carried out while they were actually decomposing over a catalyst.

It was thought that it might be possible to hydrogenate part at least of the glycol to a stable compound. The possibility of hydrogenating an unstable intermediate product of the decomposition was also considered, but thought unlikely with ethylene glycol and 1,2, propylene glycol, since previous work has shown that these decompose with loss of hydrogen. It would therefore only be possible to hydrogenate these intermediate compounds back to the glycol. The presence of a large excess of hydrogen under pressure might, however, retard the decomposition.

(1) HYDROGENATION OF ETHYLENE GLYCOL.

(a) Over Raney nickel.

This/

This has already been discussed (page 83).

(b) Over Nickel on Kieselguhr.

As Raney nickel had shown itself to be such a potent catalyst for the decomposition of the glycols, another form of nickel catalyst was prepared by reduction of nickel ammonium nitrate on kieselguhr (Covert, Connor and Adkins J. A. C. S. 1932, 1651.) Experiments were carried out to determine if this would have hydrogenating properties at a temperature below that at which it would decompose the glycol.

The catalyst was reduced for one hour at 370 - 390°C directly before use and was charged into the autoclave in an atmosphere of carbon dioxide.

The charge in the autoclave was

100 ccs. (132 gms.) Ethylene glycol.

Reduced nickel on kieselguhr catalyst containing 1.5 gms. nickel associated with 6.1 gms. kieselguhr.

Hydrogen to 1,100 lbs. per sq.inch (8 gms.)

The contents of the autoclave were stirred

during/

during the course of the reaction with the paddle stirrer in the normal position. The following graph fig. 26 shows the conditions during the hydrogenation.

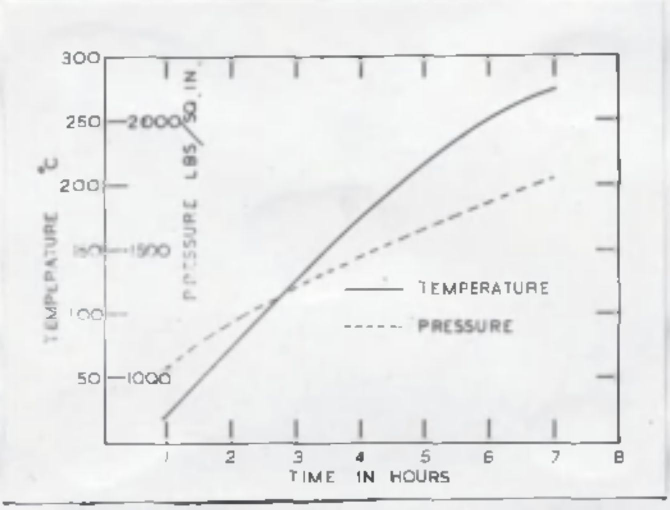


Fig. 26.

Autoclave conditions during hydrogenation
of ethylene glycol using nickel on kieselguhr.

The blow down gases (74 litres) consisted of

CO_2	3.5%
Unsats	0.5%
CO	1.5%
CH_4	26.1%
H_2	52.0%

The gas was not suitable for Podbielniak analysis owing to the low proportion of condensible matter.

The liquid products were found to be water and unchanged ethylene glycol.

It will be seen that there is no difference between the products of this hydrogenation and the hydrogenation with Raney nickel as a catalyst, which was proved to be mainly decomposition; except that the temperature required was greater, and there was less glycol decomposed. It would, therefore, seem that the nickel on kieselguhr is not so active as the Raney nickel for decomposition and that there is no hydrogenation of the glycol.

The use of this catalyst was therefore discontinued.

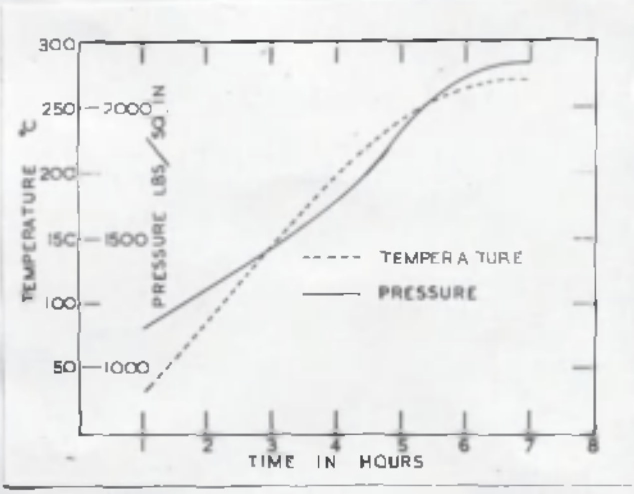


Fig. 27.

Autoclave conditions during hydrogenation of 1,2-propylene glycol.

(2) HYDROGENATION OF 1,2, PROPYLENE GLYCOL.

This was carried out under similar conditions to the hydrogenation of ethylene glycol using Raney nickel as a catalyst. For this experiment the charge in the autoclave was:-

Propylene glycol 100 ccs. (104 gms.)
Raney nickel 6.3 gms.
Hydrogen to 1,100 lbs. per sq.inch (8.8 gms.)

The charge was stirred during the course of the hydrogenation with the paddle stirrer in the normal position. The figure below gives the conditions under which the reaction was carried out (Fig. 27). It will be seen that there is a rise in pressure during the reaction; a certain amount of pyrolysis was therefore anticipated. Indeed as the table below shows, there is again very little difference between this reaction carried out in presence of hydrogen and pyrolysis carried out in a similar manner without the presence of hydrogen.

	*Hydrogenation	Pyrolysis
Gas formed	51 litres	37 litres
CO_2	4%	23.5%
CH_4	68.0%	63.0%
C_2H_6	1.4%	4.6%
H_2	18.0%	1.6%
Inert	Residue	Residue
Liquid products		
Ester (unidentified)	5 ccs.	5 ccs.
Water	20 ccs.	6.5 ccs.
Propylene glycol	15 ccs.	18 ccs.

Here again the reaction has been pyrolysis followed by the hydrogenation of the products formed.

(3) HYDROGENATION OF 2.3. BUTYLENE GLYCOL.

The hydrogenation of this glycol was carried out in a similar manner to the two preceding hydrogenations.

The charge in the autoclave was -

2,3, Butylene glycol 100 ccs. (104 gms.)
Raney nickel 8 gms.
Hydrogen to 1,100 lbs. per sq. inch
(8.8 gms.)

The contents of the autoclave were stirred in the usual manner with the paddle stirrer in the normal position. The graph shows the conditions during the course of the reaction. (Fig. 28).

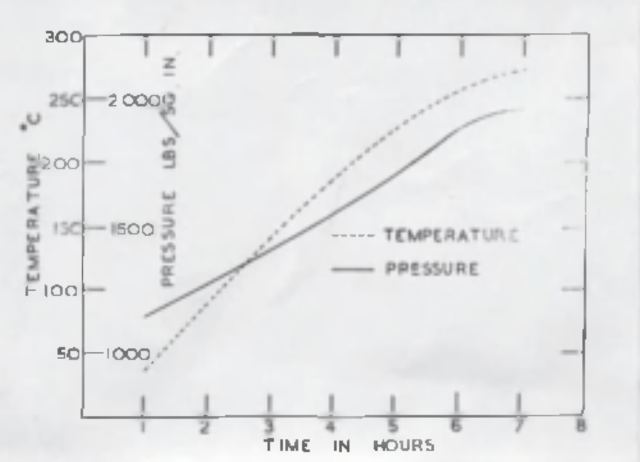


Fig. 28.

Autoclave conditions during hydrogenation of 2,3-butylene glycol.

The products of the reaction were:-

Gaseous

CO_2	0.6%
Unsats	0.4%
CH_4	51.2%
C_2H_6	3.8%
H_2	37.4%

Liquid

Methyl ethyl ketone	40 ccs. (48% yield)
Water	10 ccs.

It will be remembered that the chief product of the pyrolysis of 2,3, butylene glycol was methyl ethyl ketone so that in this case also the main reaction has been the decomposition of the glycol.

CONCLUSIONS ON THE HYDROGENATION OF THE GLYCOLS ABOVE THEIR DECOMPOSITION TEMPERATURE.

(1) It is obvious that with the catalyst used and under the conditions pertaining in the autoclave, no hydrogenation of the glycols is possible above a certain temperature as decomposition proceeds to a far greater extent than the desired hydrogenation.

(2) The presence of such large quantities of methyl ethyl ketone in the products of the "hydrogenation" of 2, 3, butylene glycol, although interesting, was disappointing, as it was expected that this compound would have been hydrogenated to sec, butyl alcohol, since it has been shown that it is possible to hydrogenate acetone at 23°C and 2 - 3 atmospheres pressure in about 11 hours using Raney nickel as a catalyst (J.A.C.S. 1932, 54, 11, 4116).

As no such hydrogenation of the methyl ethyl Ketone had been accomplished under what seemed/

seemed very vigorous hydrogenating conditions, it was suspected that the catalyst was inefficient in so far as hydrogenations were concerned, although it seemed remarkably efficient as a dehydrogenating catalyst in the decomposition of the glycols.

It has since been found that, not only was the catalyst used for these experiments inefficient, but the stirring conditions required considerable changes before a hydrogenation could be accomplished. The work on ethylene glycol has therefore been repeated with a catalyst of proved efficiency and with adequate stirring conditions without, however, making any difference in the course of the reaction or the products obtained. No further work has been done on the hydrogenation of propylene and butylene glycols above their decomposition temperature as it was thought that in this case also, the hydrogenations would follow the same course i.e. pyrolysis followed by a hydrogenation of the products of decomposition.

CHAPTER

X

THE TESTING OF CATALYSTS AND THE PREPARATION OF AN ACTIVE CATALYST.

The failure to hydrogenate methyl ethyl ketone under the conditions in which the hydrogenation of the 2,3, butylene glycol had been attempted led to a certain amount of suspicion being attached to the particular batch of Raney nickel that had been used for the work on the hydrogenation of the glycols above their decomposition temperature. This catalyst had been prepared in accordance with the instructions given by Connor and Adkins (Trans. Am. Chem. Soc. 54, 4116, 1932).

An alloy of 50% nickel and 50% aluminium is prepared and finely ground. 300 gms. of the finely powdered alloy are then added during 2-3 hours to 300 gms. of caustic soda in 1200 ccs. water surrounded by ice. When all the alloy has thus been added, the contents of the beaker are heated to 115 - 120°C with further addition of 400 ccs. 19% caustic soda solution. The contents of the beaker should be constantly stirred. When all the hydrogen/

hydrogen has been evolved, the nickel is washed free from alkali by means of distilled water and stored under alcohol.

This particular batch of catalyst had been prepared about six months previously and stored as directed under alcohol. It was still pyrophoric and, as has been shown, capable of dehydrogenating certain glycols. Its efficiency as regards known hydrogenations in the liquid phase was, however, completely untried, and it was thought that some such test should be applied.

It has been noted that the hydrogenation of acetone proceeds in the presence of Raney nickel at 23°C and 2 - 3 atmospheres pressure, the reaction being complete in about 11 hours. The containing vessel and the agitation required are not, however, specified.

This reaction was tried out in the autoclave using the old batch of catalyst.

For this experiment the charge in the autoclave/

autoclave was:-

100 ccs. acetone.
10 gms. Raney nickel.
Hydrogen to 1000 lbs. per sq.inch.

No stirring was attempted in this reaction. The autoclave was maintained at a temperature of 45 - 50°C for five hours. As no fall in pressure was noted during this time, the temperature was raised to 95 - 104°C and maintained for a further 2 hours.

When the autoclave was opened, no secondary propyl alcohol was found, indicating that no hydrogenation had taken place.

This failure of the catalyst to hydrogenate acetone confirmed the opinion that the catalyst or the conditions of hydrogenation had been at fault, and a fresh batch of 5 gms. only was prepared, and the test repeated. In this experiment as before, no stirring was attempted. The pressure was maintained at 1,000 lbs. per sq. inch, while the temperature/

temperature varied between 38 and 45°C for 6½ hours. An examination of the contents of the autoclave at the end of this time, however, revealed that no hydrogenation had taken place.

Stirring the charge with the paddle stirrer in the normal position was next attempted in an effort to hydrogenate the acetone under the same pressure, with a freshly prepared catalyst and a temperature of 50-55°C for 9½ hours, but again no hydrogenation was effected.

At this stage it was felt that too much time was being spent in putting together and dismantling the autoclave between each test and that some more simple test of the efficiency of a catalyst should be devised. It was also considered that such a test should, in the first instance be carried out in vitro to avoid any possible poisoning effects which the materials of construction of the autoclave might have on the catalyst.

The test finally used was adapted from

a test suggested by Maxted (J.S.C.I. June 1938, 197). In this test, olive oil is shaken up with the catalyst to be tested in an atmosphere of hydrogen under a slight pressure. The activity of the catalyst was determined by the amount of hydrogen absorbed in a given time under specified conditions. This method seemed, however, to require special apparatus which would have taken a great deal of time to construct, and as the activity of the catalyst was solely of interest, the test was further simplified. The hydrogen was bubbled through the olive oil and Raney nickel contained in a test-tube with a capillary glass tube fused to the foot. (Fig. 29). The whole apparatus was immersed in a beaker of boiling water and was thus maintained at a constant temperature. The absorption of hydrogen was followed by the lowering of the iodine value over a test of 15 minutes duration.

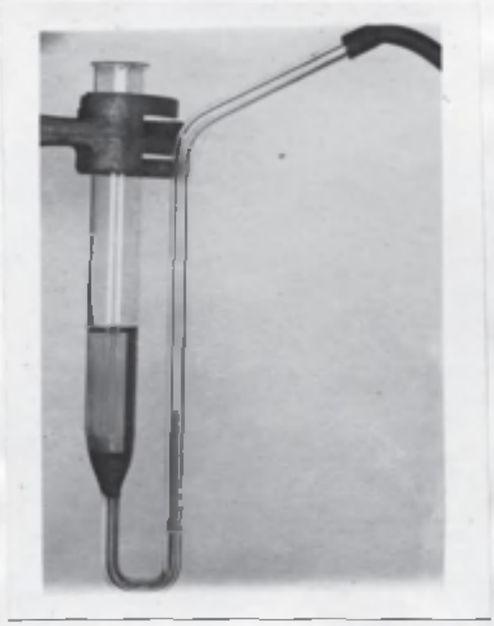


Fig. 29.

Bubbler used in measuring catalystic activity.

The method has several disadvantages.

(a) The determination of iodine values is a slow process and thus the time required for the completion of any one test is about three hours. This is a great improvement upon the time required to test out a catalyst in the autoclave, but at the same time, it makes the routine testing of a batch of catalyst before it is used in the autoclave, impracticable.

An/

An effort was made to determine the iodine value of the oil by means of a refractometer, but the change in refractive index with iodine value is not very great, and the apparatus required to maintain the refractometer at a constant temperature above the solidification point of the hydrogenated oil was too cumbersome. This method of determining iodine values was therefore abandoned.

(b) Olive oil is of uncertain composition, its iodine value and probably the ease with which it can be hydrogenated, constantly changing. Olive oil has probably been chosen by earlier workers on the testing of catalysts because of the industrial importance of the oil hardening industry, and the fact that most catalysts then made were destined for use therein. Such limitation did not apply, however, to the present case and a search was made for some organic compound which could be obtained in a pure and therefore standard condition, which could be fairly readily hydrogenated, and which had some easily recognisable property/

property which was progressively changed by the hydrogenation. Di-ethyl cinnamate and tetralin were tried but in both cases the hydrogenation was found to be too slow under the conditions pertaining.

(c) The change in iodine value is not great, and thus the determination is not highly accurate.

(d) It has subsequently been realised that,as shown by Lietz (J. Pract. Chem. 1924, 108, 52),the rate of such a hydrogenation depends upon the dissolution and diffusion of the hydrogen to the catalyst surface and not upon the rate of reaction on the surface which is, presumably, what is meant by catalytic activity. What is then being measured in such a test is this diffusion and dissolution of hydrogen. This will depend largely on two things, the agitation of the liquid, and the size and number of the catalyst particles dispersed throughout the liquid. Any variation in the change of iodine value in the following tests must/

must be attributed to this or to experimental error.

A standard test has since been described by Sully (J.S.C.I. 58, 13, 284, April 1939). In this test, the catalyst, which should contain the equivalent of 2 gms of nickel, is ground with 100 gms. of isopulegol in a paint mill. Isopulegol is used for this purpose in that it is easier to disperse the catalyst thoroughly in a hydroxylated substance. The mixture is then transferred to a pressure shaker and heated to a temperature of 70°C with hydrogen at 150 lbs. per sq. inch pressure. It is stated that the pressure of hydrogen is sufficient to prevent buffering the rate of hydrogenation by the rate of absorption of hydrogen. This is doubted, however, in view of the results of Milligan and Reid(loc cit) who showed that at atmospheric pressure it was possible to increase the rate of hydrogenation by an increase in the rate of stirring up to 13,000 r.p.m.

The test has shown, however, that it is possible to prepare an active catalyst for the hydrogenation of olive oil. The following table gives the results obtained using various catalysts.

Original iodine value of the olive oil....84

Catalyst used in test.	Iodine value after test	Activity
(1) Nil.........	83	---
(2) Original batch	84	Inactive
(3) Prepared as in (A) below	79	Active
(4) Prepared as in (B) below	78	Active
(5) Prepared as in (C) below	79	Active

(A) Materials required:

3 gms Caustic soda in 20 ccs. water
3 gms Alloy in 20 ccs. water.

The alloy and water are kept cool by surrounding with water while the caustic soda is added at such a rate that there is at no time too rapid evolution of hydrogen. When all the hydrogen has thus been added, the whole is heated on a water bath until the reaction has ceased. The Raney nickel is then washed free from alkali by means of water and the water is removed by washing with alcohol.

(B) In this method of preparation the leaching out and washing processes are carried out as in method (A) above. The catalyst is then given a final wash with 0.01 N acetic acid solution, and freed from water by washing with alcohol as before.

(C) The same quantities of starting materials are used in this case as in (A) above. The alloy is leached out at room temperature and the concentration of caustic soda was kept below 3%. The/

The reaction was, of course, a lengthy operation and the solution had to be stirred in order to prevent the alloy settling to the bottom. The leaching out occupied 68 hours, after which the catalyst was washed and dried in the same manner as (A) above.

THE WASHING OF CATALYSTS.

It will be noted that in the preparation of the above, the catalyst is always washed until the wash water is neutral. In the literature, the washing of the catalyst free from soluble salts has always been greatly stressed and insisted upon. Thus when preparing a catalyst by the double decomposition of a soluble sulphate, it is usually stated that it is essential to remove all traces of the sulphate present by washing with water, and further, that it is necessary not only to test the wash water, but also to dissolve up a portion of the catalyst and to test this also. This is probably due to the fear that the sulphate present would be reduced to sulphide, and that this sulphide would poison the catalyst.

This fear is to a large extent unjustified since it has been shown by Sully (J.S.C.I. 58, 13, 283, July 1939) that a reduced nickel carbonate catalyst prepared from nickel sulphate has a maximum efficiency so far as hydrogenation/

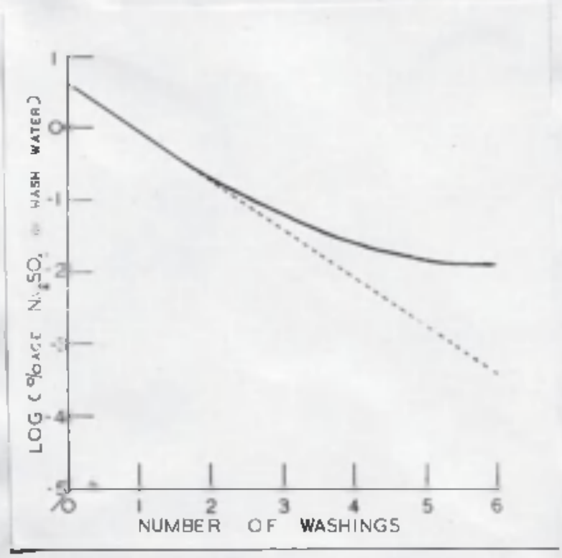


Fig. 30.

Graph showing the effect of the number of washings on the alkali present in a catalyst.

hydrogenation is concerned when the wash water, which is in equilibrium with the catalyst, removes 0.012 gms per litre sodium sulphate. The catalyst must therefore contain sulphate, and it has been further shown that part at least of this is adsorbed on the surface. For example, the following figure (Fig. 30) shows the variation between the number of washings, equilibrium between the catalyst and the wash water being established at each washing, and the concentration of sodium sulphate in the wash water expressed as a percentage.

The dotted line shows the relationship which would exist if there was no adsorption of the sulphate on the surface of the catalyst.

The washing of Raney nickel catalysts has similarly been stressed. The original reference requires the catalyst to be washed free from alkali by decantation. It would seem very difficult to remove all the alkali by this means, owing to the adsorption referred to above, and some workers (J. Bougault and Others; Bull Soc Chim 1939, 5, 1699) wash/

wash the catalyst and then neutralise it with a weak acid. Others dialyse the catalyst under a potential difference of some 220 volts.

It has been found in the College that in the hydrogenation of olive oil at atmospheric pressure, it is an advantage not to wash the Raney nickel until the wash water is completely free from alkali. For example, the following table shows the effect of the number of washings (by decantation) upon the efficiency of a Raney nickel catalyst. The activity of the catalyst is measured in the usual method (Page 128).

Original iodine value of the oil....84

Washing given to the catalyst	Iodine number of oil after test
Once...........	75
Twice..........	76
Six times......	79

There is thus a marked increase in activity of the catalyst as measured by this means if it is not/

not washed entirely free from alkali. It has been shown previously, however, see page that in all probability, the figures obtained by this means are dependent more upon the transfer of hydrogen from the gaseous phase to the surface of the catalyst. The fact that in this case the washing has decreased the apparent activity may be due to:-

(1) The washing was done by decantation. This may remove some of the very fine catalyst particles.

(2) The presence of alkali in the oil may assist in the dispersion of the catalyst.

(3) The raising of the Ph value of the oil which may alter the solubility of hydrogen in the oil and thus assist in the diffusion of hydrogen.

(4) It has been noted that, in the presence of water, Raney nickel can act as a reducing agent; a hydroxide, $Ni(OH)_2$ being formed. This oxidation may proceed to a small extent during the washing process, and it may be that this reduces the activity of the catalyst sufficient to alter the speed/

speed of hydrogenation of the olive oil.

(5) The sodium salts of the free fatty acids present may act as promoters.

CHAPTER

XI.

THE HYDROGENATION OF OLIVE OIL IN THE AUTOCLAVE.

As all the previous experiments on the hydrogenation of olive oil had been carried out in glass, it was thought desirable to determine whether any of the materials of construction of the autoclave, principally iron and monel, would have any poisoning effect upon the Raney nickel. In order to do this the material was introduced into the sample of olive oil and agitated with the catalyst for one hour at 100°C. Hydrogen was then bubbled through the oil and the activity of the catalyst measured as before by the lowering of the iodine value. The table below gives the results obtained:-

Iodine value of olive oil before test	84.

Catalyst used was prepared as in method (A) page 134.

Poison introduced	Iodine value after test
Nil....................	79.
1 gm iron filings......	79.
0.7 gms monel filings..	78.5

It will be seen that the materials of

construction/

construction used in the autoclave did not have any marked poisoning effect upon the Raney nickel. An effort was therefore made to hydrogenate the olive oil in the autoclave.

In view of the ease with which olive oil could be hydrogenated in the tests on catalytic activity at atmospheric pressure, it was disappointing to find that the oil could not be materially hydrogenated in the autoclave under the following conditions:-

Charge in the autoclave

100 ccs olive oil

3 gms Raney nickel prepared as in method (A) page 134 .

Hydrogen to desired pressure when the autoclave had reached the required temperature.

Stirring — Highest speed then obtainable (180 r.p.m.) with paddle stirrer in normal position.

Conditions

	Temperature	Pressure	Time of Contact
(1)	72°C	1000 - 725 lbs/s.i.	2 hours
(2)	102 - 107°C	780 lbs/sq.in.	1 hour

The/

The only difference between these experiments performed in the autoclave and those performed at atmospheric pressure is:-

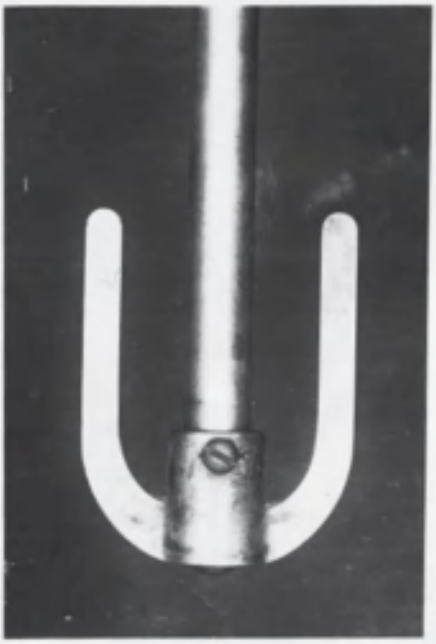
(1) The pressure. Abundant evidence is available, however, to show that increased pressure should facilitate hydrogenation.

(2) The reaction vessel. It has been shown (page 142) that the principal materials of construction used in the autoclave have no marked poisoning effect upon the activity of the Raney nickel. No trouble was therefore anticipated from this source.

(3) The stirring. It was suggested that the agitation of the olive oil in the autoclave was not so effective as in those experiments carried out at atmospheric pressure. An effort was therefore made to improve the stirring in the autoclave by lowering the position of the stirrer, and it was found that the olive oil could be hydrogenated when the stirrer was lowered to within 1/8th inch of the foot of the monel liner, the iodine value being lowered from 84 to 36 in one hour at a temperature of/

of 103 - 112°C and a pressure of 850 lbs per sq. inch.

This result shows that effective stirring in the autoclave is no less important than the activity of the catalyst.



CHAIN ?
STIRRER.

THE CHAIN STIRRER.

The paddle stirrer was set at the required distance from the foot of the monel liner by releasing the set screw and unscrewing the stirrer from the shaft, the amount of unscrewing being determined/

determined by careful measurement. This method was, however, unreliable and once or twice the stirrer jammed on the foot of the autoclave; on one such occasion the shaft was bent slightly.

A chain stirrer was therefore devised which would successfully raise the catalyst from the foot of the autoclave and agitate the liquid without damage to the shaft. Fig. (30a.)

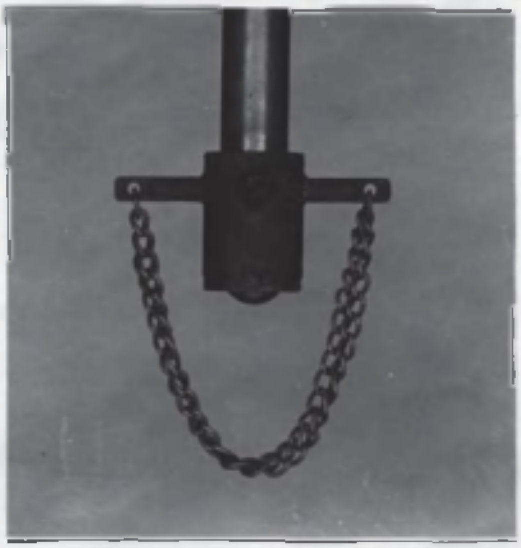


Fig. 30a.

The chain stirrer.

Using this stirrer it was found possible to lower the iodine value of the olive oil from 84 to 12 under conditions similar to those used previously. The table below gives the results obtained/

obtained with different stirrers set out for comparison:-

Original iodine value of the oil...84.

Stirrer	Time (hours)	Pressure lbs. sq. in.	Temperature	Iodine value after Test
Paddle (normal)	2	1000	72°C	84.
Paddle (normal)	1	780	102-107°C	84.
Paddle(lowered)	1	800	103-112°C	36.
Chain	1	900	80°C	12

It was noted that, after hydrogenation of olive oil with the chain stirrer, the catalyst was very well dispersed through the liquid, the nickel being in a more or less colloidal form which would not settle and which could only be removed by filtration or centrifuging. An effort was made to disperse the catalyst similarly through the oil before it was put into the autoclave, by grinding it with the olive oil in a mortar.

This treatment, however, destroyed the efficiency of the catalyst, due, either to atmospheric/

atmospheric oxidation during grinding, or else to physical contusion of the catalyst particles.

If the catalyst is dispersed in the olive oil in the autoclave in an atmosphere of nitrogen, by running the chain stirrer overnight, a remarkably efficient catalyst was obtained, it being possible to hydrogenate olive oil from an iodine value of 84 to 1.5 in one hour at 82°C and 1000 lbs. per sq. inch pressure. It is probable that oxidation of the catalyst produces the effect referred to above.

STIRRING BY BUBBLING HYDROGEN THROUGH THE LIQUID.

The stirring of the charge on the autoclave by means of hydrogen bubbled through the liquid at high pressure has also been tried. For this experiment the outlet of the high pressure booster pump was connected to the autoclave inlet system. A copper pipe was screwed into the inlet in the lid and bent so as to reach the foot of the autoclave at its axis. The pipe was secured by fastening/

fastening to the stirrer shaft after removal of the stirrer. In order to ensure that this pipe actually reached to the bottom of the liner, the latter was supported on a light spring.

The hydrogen, after bubbling through the liquid, passed up inside the liner, down between the liner and the autoclave body, and out through the drain pipe at the foot to a cooler from whence it was returned to the pump for re-circulation, see Fig. (31).

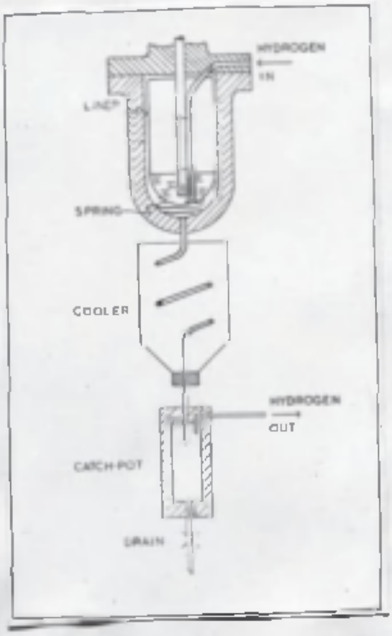


Fig. 31.

Layout of the autoclave for stirring by means of bubbling hydrogen through the liquid.

With this apparatus, however, it was found impossible to hydrogenate olive oil at 1000 lbs. per sq. inch and 100°C during one hour. Indeed an examination of the contents of the autoclave subsequently showed that the catalyst had settled on those portions of the foot of the monel liner which had been undisturbed by the bubbling of the hydrogen through the liquid.

If such a method of stirring is again contemplated, a liner must be designed which will return all the catalyst to a point on the foot of the autoclave where it can be again dispersed by the bubbling action of the hydrogen.

HIGH SPEED STIRRING IN THE AUTOCLAVE.

It has been shown by Milligan and Reid (see page 30) that the rate of hydrogenation of cottonseed oil at atmospheric pressure could be increased by increased rate of stirring. As a number of failures had been recorded due to inefficient stirring in hydrogenations in the autoclave, an effort was made to increase the speed of rotation of the stirrer shaft. As such an increase would, however, place an undue strain upon the gland owing to the side thrust from the driving belt, the shaft was supported on heavy angle irons carried on 1½" channel irons bolted to the autoclave cubicle (See fig. (32).

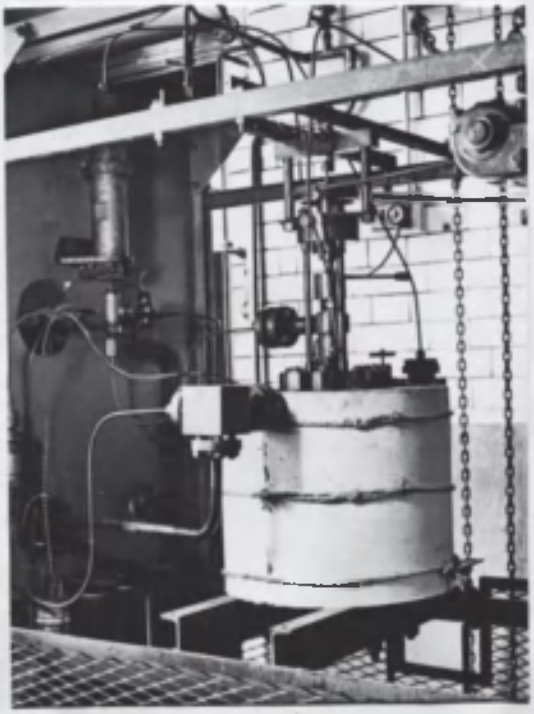


Fig. 32.
The autoclave, showing support for stirring gear.

The speed of the shaft was increased by removing the 2" pulley from the countershaft which drives the stirrer, and replacing it with a 5" pulley. The maximum speed of the stirrer shaft was therefore increased from 180 to 500 r.p.m.

The table below gives the results of these tests:-

Charge in the autoclave

100 ccs. olive oil.

3 gms.freshly prepared and active Raney nickel.

Hydrogen to 1,000 lbs. per sq. inch at 100°C.

Original Iodine value of the oil.........84.

Stirrer	Iodine value after hydrogenation for one hour at 100°C.
Paddle (normal position)	60
Chain	2.6

It will be seen that very little hydrogenation/

hydrogenation has again been effected when using the paddle stirrer in its normal, i.e. unlowered, position. This is probably due to the very heavy nature of the Raney nickel catalyst, which causes it to settle out at the foot of the autoclave. Once the particles of catalyst have reached the foot of the autoclave, no amount of stirring with the paddle stirrer appears to be able to remove them. The chain stirrer is, however, capable of disturbing and finally removing such a deposit. In this case it is to be noted that the chain stirrer is more efficient at this speed, than it was when running at 180 r.p.m. (see page 146).

Furthermore, the support for the top bearing of the stirrer shaft has greatly assisted in the keeping of the gland tight under normal running conditions, as the vibration of the shaft is greatly reduced.

CHAPTER

XII.

THE HYDROGENATION OF ALPHA GLYCOLS BELOW THE TEMPERATURE OF VIOLENT DECOMPOSITION.

It has been shown that in the presence of Raney nickel at temperatures above 230°C, the glycols decompose completely to gas even under a considerable pressure of hydrogen. The possibility of hydrogenating the glycols below this temperature was next considered. 190°C was chosen because at this temperature there was slight decomposition as evidenced by the presence of small quantities of methane in the hydrogen at the end of the reaction. The decomposition, however, did not proceed to such an extent that the hydrogen was excessively diluted or removed a large proportion of the starting material.

(1) ETHYLENE GLYCOL.

(a) Static conditions.

For these experiments the charge in the autoclave was:-

100 ccs. ethylene glycol
3 gms. Raney Nickel (freshly prepared and active)
Hydrogen to required pressure.

The charge was stirred during the course of the reaction with the paddle stirrer in the lowered position.

No notable increase or decrease in pressure occurred during the course of these experiments.

The table below gives the conditions under which each experiment was carried out and the products that were obtained.

	I	II	III
Pressure. lbs.per sq.inch	1,100	1,200	2,500
Time of Contact. Hours	4.7	2.5	5.5
Products.			
Gaseous.	37 litres	Not known	147 litres
CH_4	7.5%	3.5%	3.3%
H H_2	91%	96%	94%
Liquid.			
Ethylalcohol	1.0 ccs.	1.0 ccs.	3.0 ccs.

The actual amount of ethyl alcohol formed is, however, doubtful as in these experiments the Raney nickel was charged into the autoclave wet with ethyl alcohol in order to remove water and prevent oxidation. The approximate amount of ethyl alcohol so included in the charge (2 ccs.) has been deducted from that found at the end of the reaction to give the amounts shown in the table above.

It will be noted that the yield of ethyl alcohol is increased by increase of pressure.

(b) Circulatory Conditions.

The hydrogenation of ethylene glycol with the removal of the low-boiling products and water as formed.

It was thought that it might be an advantage to remove the volatile products and water formed in the hydrogenation of the glycol by passing hydrogen through the reaction mixture. For this purpose the same arrangement of the autoclave was used as in those experiments upon the hydrogenation of olive oil in which the hydrogen was bubbled through the liquid under pressure. (page 148.) As it has been shown, however, that the liquid and catalyst were not sufficiently agitated by this means, the chain stirrer was used in addition. The hydrogen, after passing through a cooler and catchpot from which the liquid products were removed at 2 hourly intervals, was recirculated by a booster pump through the autoclave.

The temperature chosen for the hydrogenation was lower than that chosen for the static hydrogenation so that there should be less glycol carried over in the gas/

gas stream.

For this experiment the charge in the autoclave was

200 ccs. ethylene glycol.
3 gms. freshly prepared and active Raney nickel.
Hydrogen to 1500 lbs. per sq. inch.

The contents of the autoclave were maintained at a temperature of 145 - 150°C for 30 hours during which hydrogen was passed through the liquid which was also stirred with the chain stirrer. During this time the whole of the ethylene glycol distilled over in the gas stream and was removed from the catchpot.

PRODUCTS.

The methane content of the gas slowly rose to a maximum of 2.5%, and the glycol which had passed over contained 6 ccs. of ethyl alcohol.

This low yield of ethyl alcohol is disappointing/

disappointing when the long time of contact is considered and this method does not seem therefore to possess any advantages over the static system and it was not further used.

(2) 1,2. PROPYLENE GLYCOL.

For this experiment the charge in the autoclave was:-

100 ccs. 1,2, propylene glycol
3 gms.freshly prepared and active Raney nickel.
Hydrogen to 1800 lbs. per sq. inch.

The charge was stirred with the lowered paddle stirrer, while the temperature was maintained at 185 - 192°C for five hours, the hydrogen pressure being approximately 2,400 lbs. per sq. inch.

2 ccs. of a low boiling liquid were found in the reaction products. This was found to consist of ethyl alcohol and a ketone, presumably, acetone. The gas from the hydrogenation was practically pure hydrogen containing a trace of methane.

Owing to the very low proportion of low boiling products obtained in this and in the following hydrogenation, the Raney nickel was carefully freed from alcohol by drying before use in a stream of nitrogen/

nitrogen. Tests on the catalyst before and after drying showed that this treatment had no effect upon its activity so far as the hydrogenation of olive oil was concerned. It is obvious, however, that as the catalyst is pyrophoric, stringent precautions must be taken to prevent contact with oxygen. The nitrogen was therefore passed through chromous chloride solution before use, and the catalyst was added in a stream of nitrogen.

Only 0.8 ccs. of a liquid boiling 7[illegible]-85°C was n the products of the reaction. This unidentified. The gas from the reaction s containing a little methane from the n of the glycol.

(3) 2.3. BUTYLENE GLYCOL.

For this experiment the charge in the autoclave was:-

100 ccs. butylene glycol.
3 gms. dry Raney nickel.
Hydrogen to 1900 lbs. per sq. inch

The charge was stirred during the course of the reaction with the lowered paddle stirrer for 4 hours at a temperature of 175 - 195°C. The pressure of hydrogen at this temperature was 2,500 lbs. per sq. inch.

Only 0.8 ccs. of a liquid boiling 75-85°C was obtained from the products of the reaction. This liquid was unidentified. The gas from the reaction was hydrogen containing a little methane from the decomposition of the glycol.

CHAPTER

XIII

THE VAPOUR PHASE HYDROGENATION OF ETHYLENE GLYCOL.

In view of the difficulties experienced during the hydrogenations in the liquid phase, an effort was made to hydrogenate ethylene glycol in the vapour phase by passing the vapour mixed with hydrogen over a Raney nickel catalyst. The circulating plant was unfortunately not capable of use at the time, so the autoclave was adapted for the purpose. The catalyst, which was coarse-grained Raney nickel, was supported in a monel basket about one inch above the surface of the glycol in the autoclave. It was hoped that when the glycol was heated to a temperature of 255°C, sufficient glycol vapour would be present in the hydrogen to allow hydrogenation to proceed on the surface of the catalyst. In this way the hydrogen and glycol would be presented together at the catalyst surface and no trouble would be experienced due to inadequate stirring.

This hope was justified in that the glycol vapour did come into contact with the catalyst, by which, however, it was decomposed as before, yielding finally methane and carbon dioxide. No ethane or ethyl/

ethyl alcohol was detected in the products of the reaction.

The table below gives the analysis of the gas present at the end of the reaction in which the hydrogen pressure was 1,700 lbs. per sq. inch.

CH_4	76.0%
H_2	20.0%
CO_2	2.5%

No further work was done upon this aspect of hydrogenations since, as shown here, the temperature required to vapourise the glycol under the considerable hydrogen pressure present is so high that the glycol decomposes in the presence of the catalyst.

CHAPTER

XIV.

THE HYDROGENATION AND PYROLYSIS OF GLYCEROL.

It has been stated that glycerol can be hydrogenated to give 2,3, propylene glycol at temperatures above 150°C and at pressures of 70-100 atmospheres. The catalyst recommended for the work are those of the iron and platinum groups; copper, silver, tungsten and gold, which may be mixed with each other or with a support as desired (I.G. Farbenhind. British Patent, 299,373. Oct. 24th, 1927).

In view of the fact that much of the previous work on hydrogenation has been obscured by pyrolysis reactions, this aspect of the work was considered first.

Will (Chem. Zentr. 1906, 11, 1,000; 11, 199.) has observed that either di-glycols or poly-glycols result when glycerol is heated for 7 - 8 hours at a temperature of 290 - 295°C.

If, on the other hand, the glycerol vapours are passed over a glowing platinum spiral; formaldehyde, acetaldehyde, glyoxal and acrolein are formed (Trillat Bull/

Bull. Soc. Chim. 3, 29, 42, 1903.)

The most thorough investigation of the products of the pyrolysis of glycerol has, however, been made by Nef (Ann 1904, 335.)

He observed considerable decomposition at 430 - 450°C in a tube packed with pumice. The glycerol is therefore less stable towards heat than are the glycols which normally require a temperature of 550°C for decomposition over pumice. Decomposition of the glycerol proceeded at such a rate that 250 gms. of reaction product passed through the hot tube in 16 hours.

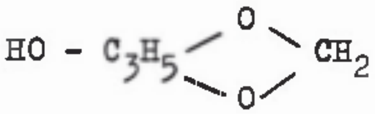
The liquid obtained from this represented 90% of the original material and consisted of

(1) 28.8 gms. of a volatile portion containing formaldehyde, acetaldehyde and acrolein.

(2) 48 gms. of a 20% solution of hydroxy-acetone in water (Boiling-point 23-40°C).

(3) 9 gms of pure hydroxy-acetone (Boiling-point 40 - 60°C).

(4) 25.1 gms. of a mixture of formaldehyde-glycerol,



acetaldehyde-glycerol, and acrolein-glycerol (Boiling-point 75 - 110°C).

(5) 66 gms. unchanged glycerol.
(6) 11.4 gms. residue.

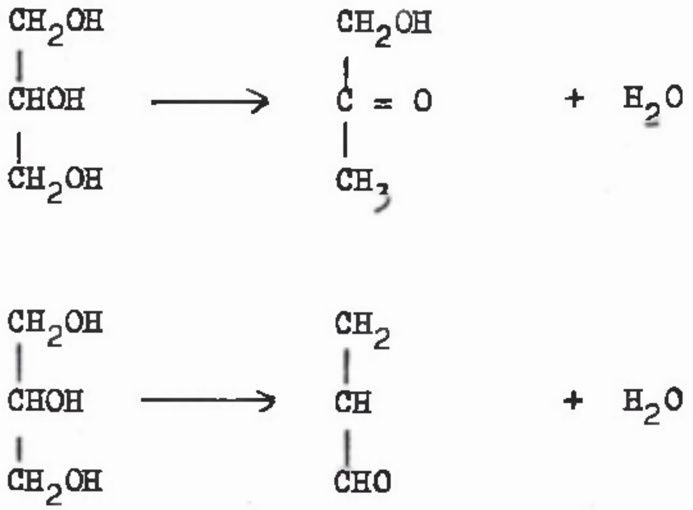
About two litres of gas were obtained having the following composition:-

CO	85.9%
H_2	14.1%

Graphite was also reported as being present in the cracking tube.

The mechanism suggested for this pyrolysis was

CH/



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2OH \\ | \\ C = O \\ | \\ CH_3 \end{array} \quad + \quad H_2O$$

$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2 \\ | \\ CH \\ | \\ CHO \end{array} \quad + \quad H_2O$$

Followed by condensation and polymerisation.

PYROLYSIS UNDER PRESSURE IN THE PRESENCE OF RANEY NICKEL.

As the hydrogenation of the glycerol was to be performed in the autoclave under high hydrogen pressures in the presence of Raney nickel, the pyrolysis of the glycerol was studied under similar conditions. As any nitrogen introduced at the beginning would mask any products of the reaction, no initial gas pressure was present in the autoclave.

The charge was:-

120 gms. glycerol.
4 gms. Raney nickel (Twice washed only).

The course of the reaction is as shown in Fig. (33). There was considerable increase in the pressure when the contents of the autoclave reached 255°C.

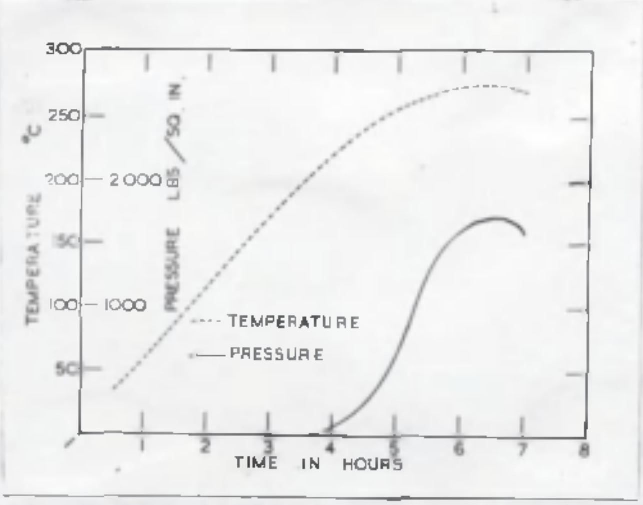


Fig. 33.

Autoclave conditions during pyrolysis of glycerol.

The gas from the reaction (50 litres) consisted of

CO_2	44.2%
Unsats	1.6%
H_2	8.1%
CO	1.1%
CH_4	35.2%
Residue	Inert.

The liquid product separated on standing into two layers, as follows.

(1) Lower aqueous layer.

This was found to consist of approximately 3 ccs. of a mixture of acetone and alcohol together with water. That the low-boiling constituents of this layer were acetone and alcohol was proved as follows:-

(a) reaction with sodium.
(b) precipitate with 2, 4-dinito-phenylhydrazine.
(c) gives formaldehyde reaction.

(2) Upper layer insoluble in water and soluble in ether. This was divided into the following fractions by normal distillation i.e. without a fractionating column.

(a) 0 - 100°C, 5 ccs.
(b) 110 - 200°C, 15 ccs.
(c) 200 - 270°C, 15 ccs.
(d) 120 - 170°C at 5 mm pressure, 8 ccs.
(e) 170 - 200°C at 5 mm pressure, 5 ccs.

The constitution of these various fractions was not further examined as they were not found in the products/

products of hydrogenation of glycerol. They are interesting, however, as those in the upper layer do not seem to be hydroxylated compounds as they are insoluble in water and soluble in ether. Attempts have been made to hydrolyse them in the belief that they might be esters, but without success. The higher fractions, indeed, seemed to have lubricating properties which may prove of value.

The pyrolysis under pressure in the presence of Raney nickel, bears no relationship apparently, to those pyrolyses of glycerol performed by Nef and others, reported previously in that heavy hydrocarbon-like bodies and no hydroxy-acetone have been found in the products.

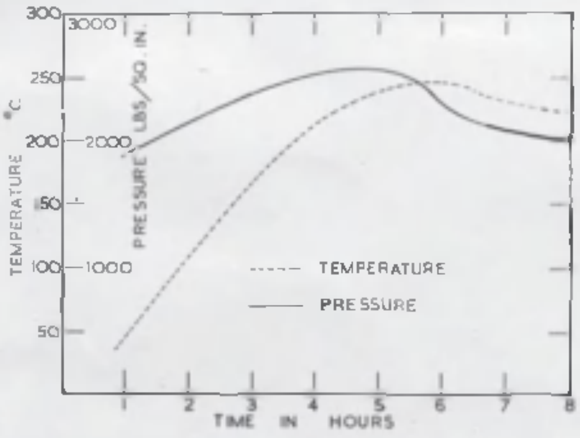


Fig. 34b.

Autoclave conditions during hydrogenation of glycerol. 2.

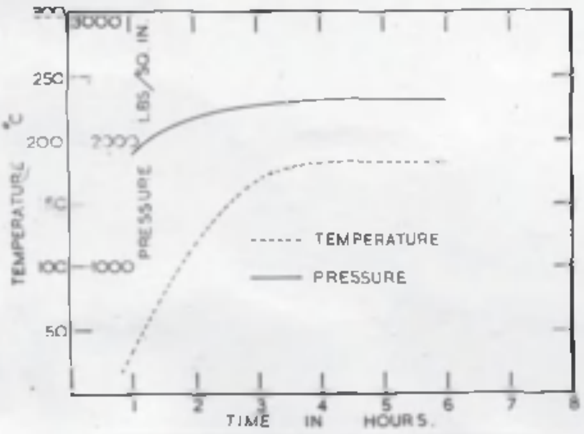


Fig. 34c.

Autoclave conditions during the hydrogenation of glycerol. 3.

THE HYDROGENATION OF GLYCEROL.

For these experiments the charge in the autoclave was:-

100 ccs. Glycerol.
4 gms. Raney nickel (Alcohol wet)
Hydrogen to required pressure.

The accompanying graph shows the conditions pertaining during each of three experiments. These are considered in detail below, Fig. (34).

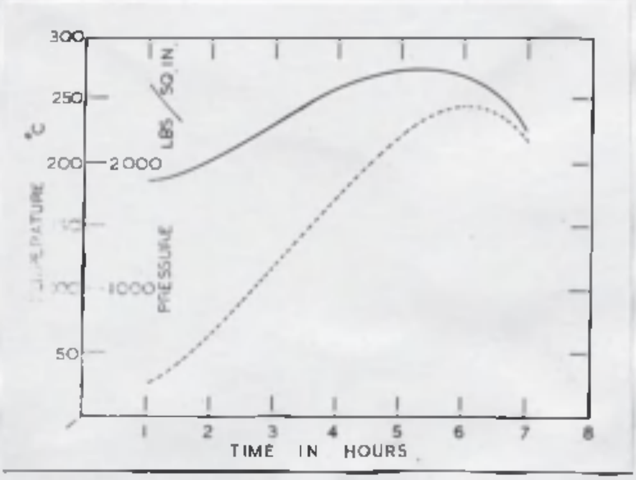


Fig. 34a.

Autoclave conditions during hydrogenation of glycerol. 1.

(1) In the first of these the paddle stirrer was/

was used in the lowered position for the agitation of the liquid. The temperature of reaction was purposely kept low in order to minimise the decomposition of the glycerol. No product except glycerol was found in the liquid products at the end of the reaction. The gas from the reaction contained 97% hydrogen.

(2) In this experiment the chain stirrer was used and the temperature was raised to 230°C. The products from the reaction were

Gaseous (approximately 100 litres)

CO_2	3.5%
H_2	65%
Ethane	1.5%
CH_4	28.0%

Liquid

Water	29 ccs.
Propylene glycol	25 ccs.

In this experiment, glycerol had been used for the lubrication of the gland in order to obviate any confusion as to the final products obtained. That the product was actually propylene glycol was demonstrated by the following comparison between it and a sample of pure 1,2, propylene glycol.

Characteristic	Product	1,2, Propylene glycol.
Boiling-point	180 - 200°C	183°C.
Refractive index	1.425	1.428
M.Pt. of the 3,5, dinitro-benzoate.	123°C	123°C
Mixed M.Pt. of above two.	123°C	

Furthermore, the gaseous products are far in excess of those that would be expected from the pyrolysis of the glycerol alone. It is probable then that the major portion of this gas has been formed by the decomposition of some of the propylene glycol formed by hydrogenation. Comparison between the gas obtained here and the gas obtained from the hydrogenation of propylene glycol above its decomposition temperature (page 117) will show that this is probably so.

CONCLUSION.

It is possible to hydrogenate glycerol to give a fair yield of 1,2, propylene glycol within a narrow temperature range. Moreover, this propylene glycol is formed by hydrogenation, as neither the glycol, nor its decomposition products are to be found as products of the pyrolysis of the glycerol.

CHAPTER

XV.

HYDROGENATION AND PYROLYSIS OF LAEVULOSE (FRUCTOSE)

PREVIOUS WORK.

Previous work has shown that under suitable conditions it is possible to hydrogenate laevulose to give mannitol at temperatures ranging from 80 - 130°C and under considerable hydrogen pressures.

If hydrogenation is carried out a higher temperatures of 160 - 180°C, reduction is carried a stage further to give methyl alcohol, ethyl alcohol, and various glycols. (Zartmann and Adkins. J. A. C. S. 1933, 55, 4559.)

No reference can be obtained to the products of the pyrolysis of laevulose.

PYROLYSIS.

This was considered first, and the reaction carried out in the autoclave in the presence of Raney nickel/

nickel. Considerable nitrogen pressure was present during the experiment in order to prevent excessive decomposition and since it was not anticipated that the gas from either the hydrogenation or the pyrolysis of the laevulose would contain any important constituents. The dilution of the gas would, therefore not be a matter of great concern.

The charge in the autoclave was:-

50 gms. Laevulose.
50 ccs. Water.
3 gms. Freshley prepared Raney nickel.
Nitrogen to 1,000 lbs. per sq. inch.

The charge was stirred during the course of the reaction by means of the chain stirrer running at 500 r.p.m. The temperature of the autoclave was raised to 142°C and maintained at this temperature for 4½ hours.

PRODUCTS.

When cold, the autoclave was opened and the contents examined. Nothing distillable, except water, was/

was, however, obtained, the product being principally carbon and water.

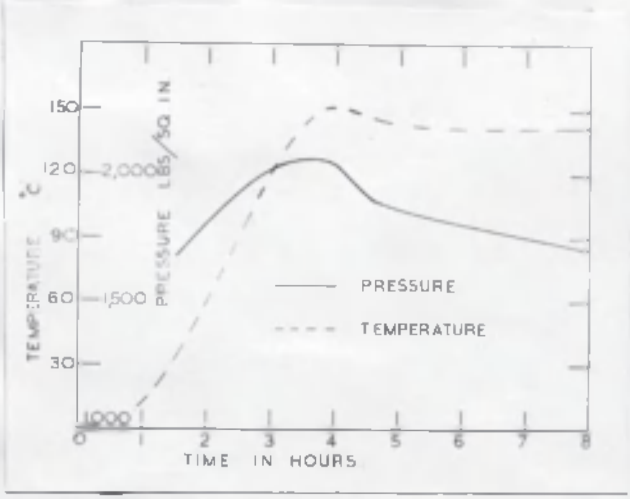


Fig. 35.

Autoclave conditions during hydrogenation of laevulose. 1.

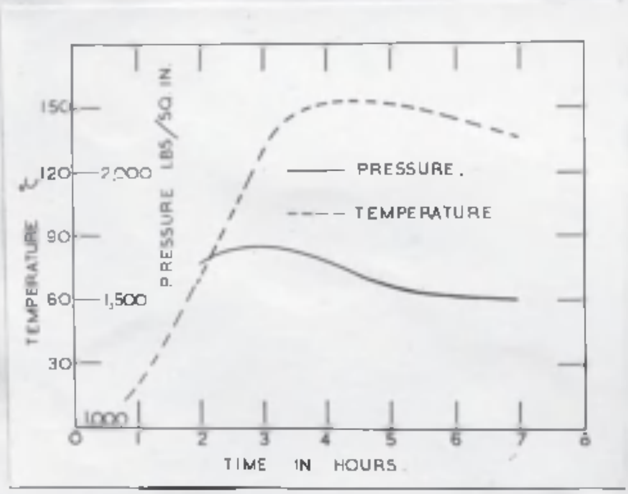


Fig. 36.

Autoclave conditions during hydrogenation of laevulose. 2.

HYDROGENATION.

Two attempts have been made to hydrogenate laevulose. In both of these the charge in the autoclave was:-

100 gms. Laevulose.
100 ccs. water.
3 gms. Freshly prepared Raney nickel.
Hydrogen to maximum pressure obtainable.

The accompanying graphs (Figs. 35 & 36) show the conditions under which the reaction was carried out. The charge was stirred by means of the chain stirrer running at 500 r.p.m.

It is to be noted that in this experiment, the gland was lubricated by means of glycerol. This is unfortunate as it meant that any glycerol or hydrogenation products thereof found in the products of reaction must be viewed with suspicion, as they may have come from a leak in the gland (see page 47). The only satisfactory lubricants which have been tried in/

in the laboratory were, however, ethylene glycol, 1,2, propylene glycol, glycerol, and olive oil; glycerol was chosen as the most satisfactory of these for the present purpose.

Both the graphs obtained show a considerable absorption of hydrogen as evidenced by the fall in hydrogen pressure. It was thus suspected that some hydrogenation had taken place.

PRODUCTS.

The liquid from the second hydrogenation crystallised out spontaneously and gave finally a yield of 40 gms. pure mannitol. That the product was actually mannitol was proved by the preparation of the acetyl derivative m.Pt.

119 °C

The liquid from the first hydrogenation did not, however, crystallise out, and as it was not then known that it would contain mannitol, it was not seeded with the appropriate crystal. It was therefore distilled, the final fraction being distilled under a high vacuum. This gave three fractions:-

(a) B.Pt. 180 - 220°C at atmospheric pressure. This was found to contain small quantities of ethylene glycol. 3 ccs.

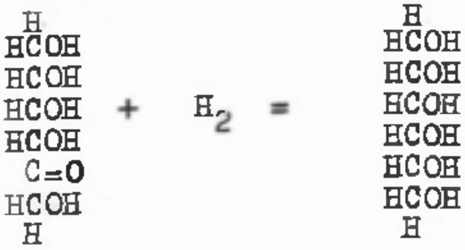
(b) B.Pt. 220 - 270°C at atmospheric pressure. This fraction was suspected to contain glycerol, but no acrolein could be detected on heating the compound with $KH(SO_4)$ 8 ccs.

(c) B.Pt. 270 - 300°C. This contained mannitol, which, however, could not be made to crystallise out, presumably because of impurities present.

15 ccs.

The mechanism of the hydrogenation to ethylene glycol is thought to be:-

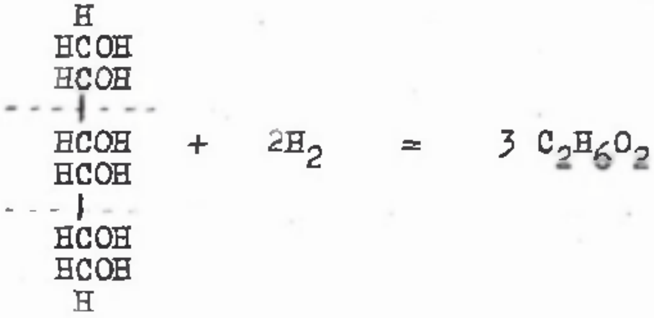
(1) The hydrogenation of the laevulose to give mannitol



$$\begin{array}{c}\mathrm{H}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{C{=}O}\\ \mathrm{HCOH}\\ \mathrm{H}\end{array} + H_2 = \begin{array}{c}\mathrm{H}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{H}\end{array}$$

(2)/

(2) The subsequent fissure of this molecule between two pairs of carbon atoms.



$$\begin{array}{c}\mathrm{H}\\ \mathrm{HCOH}\\ \mathrm{HCOH}\\ \hline \mathrm{HCOH}\\ \mathrm{HCOH}\\ \hline \mathrm{HCOH}\\ \mathrm{HCOH}\\ \mathrm{H}\end{array} \quad + \quad 2H_2 \quad = \quad 3\ C_2H_6O_2$$

These experiments confirm the results of previous work which has been done on the subject in that it has been shown that laevulose can be hydrogenated to give mannitol in considerable yield. No time has been available to show the effect of increased temperature on the hydrogenation of the mannitol produced, though from the small quantities of ethylene glycol found in the products of the above reactions, it would seem that this would follow the lines indicated by previous work i.e. hydrogenation to glycerol and glycols.

SECTION IV.

CONCLUSIONS.

CHAPTER

XVI.

CONCLUSIONS.

1. The work done in the College and reported here has shown principally how to prepare an efficient catalyst and make use of this catalyst in the autoclave. A great deal of time has been spent upon this aspect of the work, but this was unavoidable, as it is obvious that the plant and catalyst used must be made efficient and shown capable of performing hydrogenations before any work could be reported on the hydrogenation of hydroxy compounds.

Time has also been spent upon the designing and perfecting of the various gas and liquid analysis units that were used in the work.

2. The work on the hydrogenation of hydroxy compounds has shown that:-

(a) From the review of the literature given previously, it would seem impossible to hydrogenate a hydroxy compound containing only one hydroxyl group to a hydrocarbon/

hydrocarbon unless the compound is of very high molecular weight, or else contains a benzene ring.

It has been shown for instance that it is possible to hydrogenate benzyl alcohol to toluene by passing the vapour and hydrogen at 375°C and atmospheric pressure over nickel (Bull Soc. Chim. 33, 616, 1905.) and that it is possible to hydrogenate phenols to hydrocarbons at 70 - 80 atmospheres pressure at 180°C over alumina. (Kling and Florentin. Comptes Rends. 1927, 184, 885.)

(b) This review also indicates that compounds containing two hydroxyl groups which are not on adjacent carbon atoms can be hydrogenated to alcohols under considerable pressures and at temperatures of 250°C in the presence of certain catalysts (Connor and Adkins. J. A. C. S. 54, 4678, 1932).

(c) The work done in the College and reported here has shown that when a hydroxy compound contains two hydroxyl groups on adjacent carbon atoms, hydrogenation will not proceed since the temperature required/

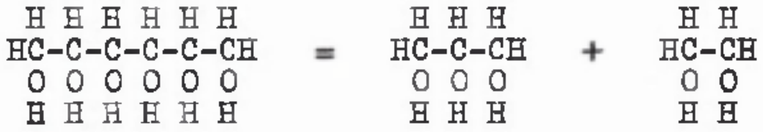
required for hydrogenation is so high that the compound will decompose in the presence of the catalyst used for hydrogenation. For example, it has been shown by Connor and Adkins (above) that the temperature required for the hydrogenation of 1,3 propylene and butylene glycols is about 250°C in the presence of a copper chromite catalyst. The work done in the College has shown that 1,2 ethylene, 1,2 propylene, and 2,3 butylene glycols will decompose rapidly at such temperatures when in the presence of a hydrogenating catalyst.

(d) When more than two hydroxyl groups are present on adjacent carbon atoms, hydrogenation may proceed so that two hydroxyl groups on adjacent carbon atoms are finally left. It has been shown here and elsewhere that glycerol may be hydrogenated to give 1,2 propylene glycol, but not 1,3-propylene glycol.

The hydrogenation of these last two remaining hydroxyl groups is a much more difficult operation than the hydrogenation of the other groups.

(e) In the case of compounds containing a large number/

number of hydroxyl groups, there is an abundance of evidence to show that hydrogenation will proceed so that the compound is broken down in the first instance, none of the hydroxyl groups being reduced.



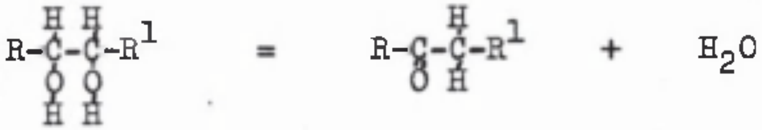
$$\begin{array}{c}\mathrm{H\ H\ H\ H\ H\ H}\\ \mathrm{HC{-}C{-}C{-}C{-}C{-}CH}\\ \mathrm{O\ O\ O\ O\ O\ O}\\ \mathrm{H\ H\ H\ H\ H\ H}\end{array} = \begin{array}{c}\mathrm{H\ H\ H}\\ \mathrm{HC{-}C{-}CH}\\ \mathrm{O\ O\ O}\\ \mathrm{H\ H\ H}\end{array} + \begin{array}{c}\mathrm{H\ H}\\ \mathrm{HC{-}CH}\\ \mathrm{O\ O}\\ \mathrm{H\ H}\end{array}$$

A hexose is first reduced to the saturated alcohol stage. In the College it has been shown that mannitol may be formed by the hydrogenation of laevulose. Previous work has shown that further hydrogenation under more rigorous conditions will disrupt the alcohol to give simpler alcohols such as erithritol, glycerol, and ethylene glycol. These alcohols may be further reduced under the conditions given in (d) above to give a-glycols which may decompose.

3. The work which has been done on the Pyrolysis of hydroxy compounds may be generalised as follows:-

(a)/

(a) In the absence of catalysts, compounds containing two hydroxyl groups on adjacent carbon atoms, decompose with the elimination of water to give an aldehyde or ketone

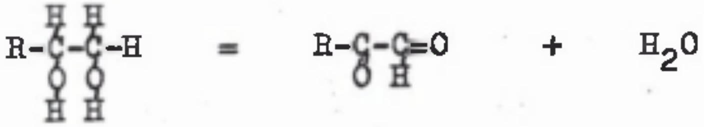


$$R-\overset{H}{\underset{\substack{O\\H}}{C}}-\overset{H}{\underset{\substack{O\\H}}{C}}-R^1 \quad = \quad R-\underset{O}{C}-\overset{H}{\underset{H}{C}}-R^1 \quad + \quad H_2O$$

The aldehyde or ketone may further decompose.

The temperature required for this decomposition is normally above 500°C

(b) In the presence of hydrogenating catalysts, compounds having two hydroxyl groups on adjacent carbon atoms at the end of a chain, decompose by losing hydrogen with either the formation of a glyoxal derivative, or else the complete disruption of the molecule.



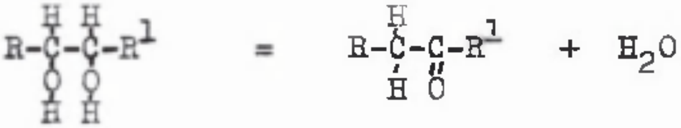
$$R-\overset{H}{\underset{\substack{O\\H}}{C}}-\overset{H}{\underset{\substack{O\\H}}{C}}-H \quad = \quad R-\underset{O}{C}-\underset{H}{C}=O \quad + \quad H_2O$$

This decomposition will take place at much

lower/

lower temperatures than the decomposition without catalysts.

(c) In the presence of certain catalysts, compounds having two non-terminal hydroxyl groups on adjacent carbon atoms decompose with the elimination of water to give ketones:-



$$R-\underset{\underset{H}{O}}{\overset{H}{C}}-\underset{\underset{H}{O}}{\overset{H}{C}}-R^1 \quad = \quad R-\underset{H}{\overset{H}{C}}-\underset{\overset{\|}{O}}{C}-R^1 \quad + \quad H_2O$$

(d) The pyrolysis of those compounds containing two hydroxyl groups which are not on adjacent carbon atoms, has not been attempted in this work, but it would seem from the literature available that this type of compound is more stable than that which has hydroxyl groups on adjacent carbon atoms. (Hurd, "Pyrolysis of Carbon Compounds" p. 180). This is also shown by the fact that it is possible to hydrogenate 1,3 propylene and butylene glycols at temperatures of 250°C in the presence of copper chromite catalysts, (Connor and Adkins J.A.C.S. 54, 4678, 1932) whereas at this temperature it has been shown that glycols having hydroxyl groups on adjacent carbon atoms, decompose rapidly in the presence of nickel catalysts.

CHAPTER

XVII.

SUGGESTIONS FOR FUTURE WORK.

(1) On the subject of hydrogenation generally.

A great deal of research still requires to be done on the influence of temperature, pressure, stirring, and solvent upon the rate of hydrogenation reaction.

It has been pointed out in a previous chapter that a hydrogenation reaction in reality consists of several physical as well as chemical reactions, and that in all probability these physical reactions are slower than, and are thus more important than, the chemical reactions.

For example, the influence of pressure upon those hydrogenation reactions in which there is no decrease in volume must be doubtful. It has been noted elsewhere in this thesis that previous workers have considered pressure to be essential to a number of hydrogenation reactions because of the increase in the solubility of hydrogen in the liquid phase. It is obvious/

obvious, however, that if this is so, it would be quite possible to carry out the reaction at a lower pressure, provided that some suitable solvent be found in which the hydrogen is sufficiently soluble, and adequate stirring conditions are used.

Milligan and Reid (loc cit) have shown that the rate of hydrogenation of cottonseed oil at atmospheric pressure is proportional to the rate of stirring up to 13,000 r.p.m.

These results should be confirmed at high pressures, and at the same time an attempt should be made to determine the maximum possible speed of any hydrogenation i.e. the speed of the actual chemical reaction when it is not buffered by the physical reactions. It is only when this maximum speed of hydrogenation is reached that figures proportional to the activity of a catalyst for the purposes of hydrogenation can be obtained.

(2) RECOMMENDED FUTURE WORK ON THE HYDROGENATION OF HYDROXY COMPOUNDS.

Once the optimum conditions of hydrogenation have been fully investigated, it will be possible to attempt the hydrogenation of the sugars and determine whether the work done by previous workers and reported previously is accurate.

It may then be possible to alter conditions such that, in place of disruption, more or less complete hydrogenation of the molecule may be effected.

SECTION V.

ADDENDA.

CHAPTER

XVIII.

AMENDED DESIGN OF A HIGH PRESSURE PLANT.

Various criticisms have been expressed in this thesis about the design of the autoclave. Actual operation over a long period has shown how many minor details could be improved.

Many such improvements have actually been made during the course of the work. Others could not have been made owing to the very great changes required, which would have necessitated the cessation of the work for a fairly lengthy period. It was thought, however, that these alterations should be incorporated in the design of an autoclave which would serve, along with that of the present autoclave as the basis of the design of any future plant.

The design of the autoclave itself is as shown in Blue-print No. (2) (in back pocket). The main differences between this design and that of the present autoclave (Blueprint No. 1) are as follows.

(1) The gas entrances and exits.

These/

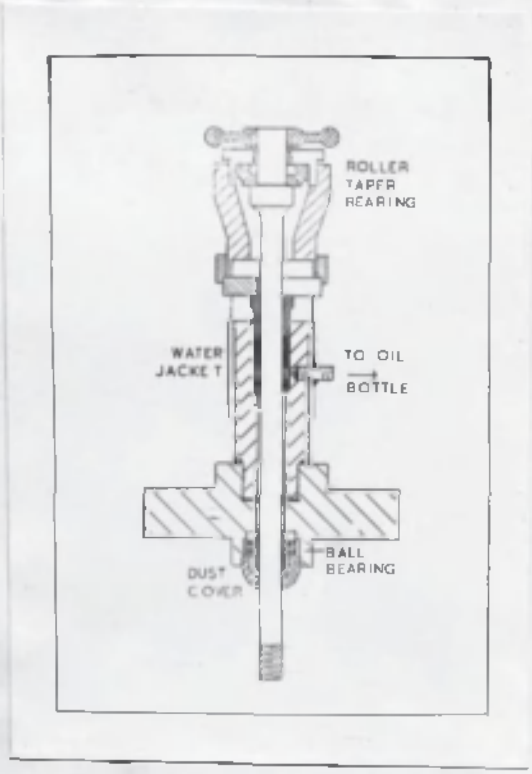


Fig. 36.

Suggested design for an autoclave stirrer shaft.

These are screwed into the flange of the body of the autoclave instead of into the lid. By such an arrangement, these joints need not be broken and made every time the autoclave is opened. This would result in a great saving of time, and would obviate the possibility of these joints leaking after being continually disturbed.

(2) The form of the gland and stirrer.

The gland and stirrer have been entirely remodelled. It has been pointed out previously that the top support for the autoclave stirrer shaft is inadequate, and that the whole should be made more rigid. Further it has been suggested that the shaft should be supported both above and below the gland, so that there is no possibility of straining the gland and causing leakage.

The form of the gland is shown in fig. (36) the whole gland and top bearing are carried in one gland pillar. In the top of this pillar is situated a wide angle roller taper bearing which takes the axial thrust due to the pressure in the autoclave, and at the same time centralises the shaft. The outer housing/

housing for the bearing is screwed into the gland pillar so that, when the stirrer shaft is to be removed, this housing may be unscrewed and the shaft lifted out. The housing should be held rigid by any of the well-known methods.

That part of the shaft below the gland is carried on a self-aligning ball race carried in the lid of the autoclave. This ball race is fastened to the shaft by means of a withdrawal taper sleeve, and it is therefore recommended that the shaft below this point should be cut away for a few thousandths of an inch so as to allow easy removal of the shaft from the race.

As some provision must be made for the protection of this ball-bearing from the vapours and catalyst particles present in the autoclave, a dust cover is fitted. This dust cover is screwed into the lid of the autoclave and also serves to secure the outer housing of the ball-bearing. A felt washer gland is fitted between the dust cover and the shaft. This gland is not intended in any way to keep back pressure, but it should prevent an undue quantity of vapours and debris from entering and damaging the bearing/

bearing.

The gland itself is of the lubricated lantern ring variety, which may be fitted with a spring in place of the lantern ring (see page 53). Tightening is done by means of a threaded ring screwed on the outside of the gland pillar, the pressure from this ring being transmitted to the gland by means of a bridge. This is so constructed that the gland may be entirely released by unscrewing the tightening ring a few threads and removing the bridgepiece. The gland packing may then be removed through the opening in the top of the gland pillar by means of a suitable extractor.

The gland is cooled by a water jacket which entirely surrounds the gland packing. In order that this may be so, the gland tightening ring and the lubricant inlet must be screwed into position before the water jacket is soldered on.

CHOICE OF PACKING AND THE MAXIMUM SPEED OF ROTATION OF THE SHAFT.

Much has been said in this thesis about the desirability/

desirability of high speed stirring, and it was thought that in any design of autoclave put forward here, provision should be made for the stirring of the contents at a maximum speed of not less than 2,000 r.p.m.

For this purpose, the support of the stirrer shaft has been made exceptionally strong and rigid, the stirrer shaft has been supported below the gland as well as above, and all parts of the stirrer mechanism should be properly balanced.

Now there are two factors that limit the rate of rotation of a shaft running through such a gland.

(1) The vibration of the moving parts. This has already been dealt with above.

(2) The temperature of the gland. The maximum temperature permissible will, of course, vary with the nature of the packing used. This temperature will furthermore be governed by the following factors:-

(a) The speed of rotation of the shaft.

(b)/

(b) The coefficient of friction between the packing and the shaft when the packing is compressed to a degree sufficient to prevent undue leakage through the gland.

(c) The heat transfer co-efficient from the inner surface of the gland to the water jacket. This last may be considerably increased and the temperature of the gland thus lowered by placing gunmetal rings in the packing. These gunmetal rings will serve to conduct heat away from the shaft. Their size and number must be chosen from a consideration of the size of the gland and the desired heat conductivity. They should be plain i.e. unchamfered.

Once the maximum operating temperature of the gland and its heat transfer characteristics have been decided upon and determined, it will be possible to determine the total heat transferred from the shaft through the gland to the water jacket. If the autoclave is cold at the time, i.e. no heat is being conducted up the stirrer shaft, this quantity of heat cannot be greater than the heat equivalent of the work done in driving the stirrer shaft.

The/

The stirrer shaft then, may be rotated at such a speed that work is done on it equivalent to this quantity of heat.

The shaft is driven from above to obviate the side thrust that would result from the use of a belt drive. (See blueprint No. 3 in back pocket). The motor and variable speed drive are mounted on a carriage above the autoclave. The carriage is on wheels so that it may be removed to one side when the autoclave lid is to be raised. Provision must be made for the accurate location of the drive over the center of the stirrer shaft.

The actual drive between the change speed pulley and the shaft is by a rod splined at both ends so that it may be removed easily. Silentbloc, (rubber) bushes are inserted between the rod itself and the male portions of the splines so that a little lateral movement of the driving gear is permissible.

THE STIRRER.

In order fully to make use of the high speed

of/

of stirring that would be available in this form of autoclave, a new type of stirrer has been designed. See Fig. (37).

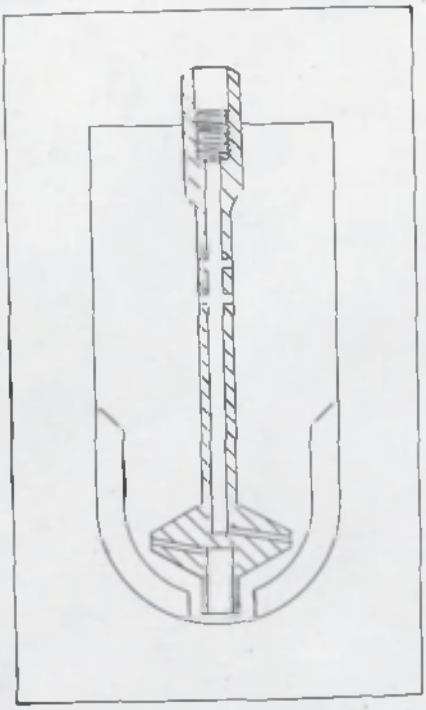


Fig. 37.

High speed stirrer.

This stirrer was adapted from a design by Milligan and Reid (loc cit). It is intended thoroughly to mix the liquid to be hydrogenated, the catalyst, and the hydrogen present in the autoclave. In/

In form it is a double centrifugal pump drawing catalyst and liquid from the foot of the autoclave liner, and at the same time hydrogen from the vapour space, and delivering them together at the periphery of the disc. A special shape of liner must be used in order to prevent the swirling of the main body of the liquid.

THE OIL BOTTLE.

The oil bottle is fastened to the wall of the autoclave cubicle. The design of the oil bottle has furthermore been changed so that it can be refilled without breaking any pipe joints or removing the bottle from the wall.

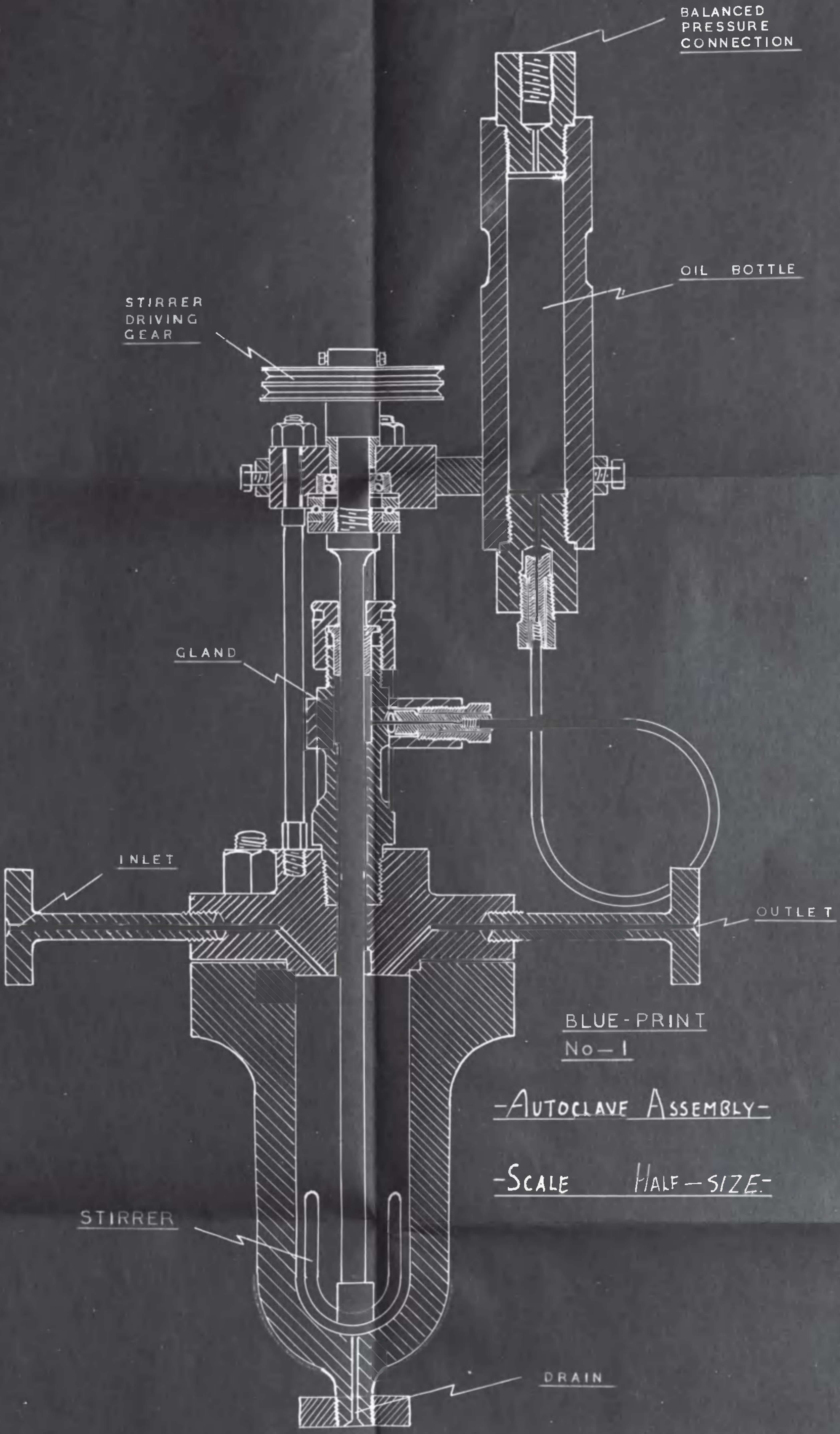
TEMPERATURE INDICATORS.

These should be by thermocouple and millivoltmeters as before, but the use of a hollow stirrer shaft for the purpose should be discontinued, and/

and the thermocouple junction should be placed in some more secure and accessible place. The actual position of this will furthermore depend upon the final choice of stirrer, as it is obvious that there must be a suitable clearance between these two. No thermocouple is therefore indicated in the drawings of the autoclave. A thermocouple should also be placed in the heater block as before. No thermocouples should be welded on to the sides of the autoclave body.

Finally it is to be emphasised that none of the drawings here given are intended to be final, as both the design, size and material of construction of the autoclave will have to be chosen to suit the actual experimental conditions envisaged. It is hoped, however, that they will serve as a useful guide in future designs of a similar high pressure plant.

BLUE-PRINTS →



BLUE-PRINT No-1

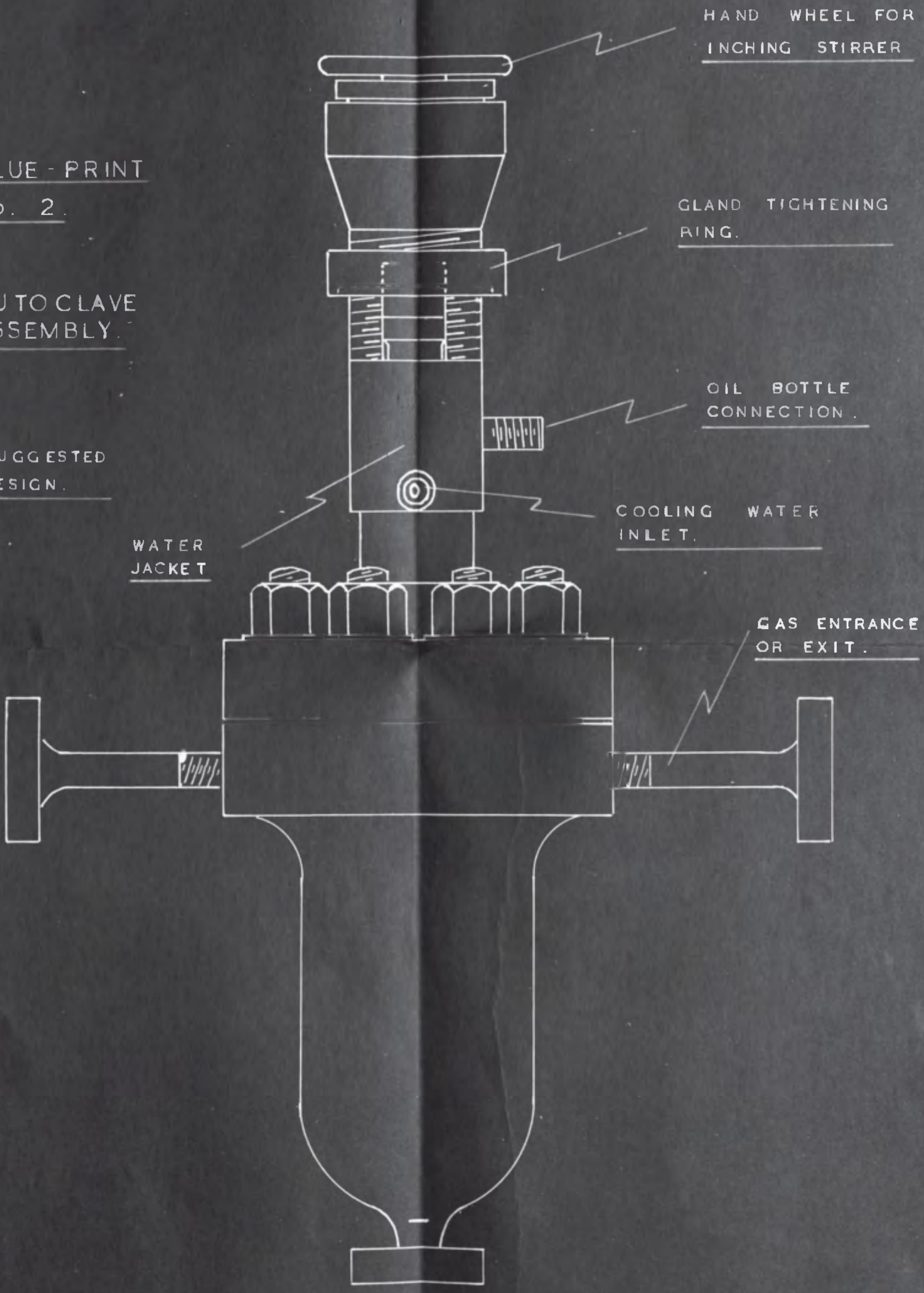
-AUTOCLAVE ASSEMBLY-

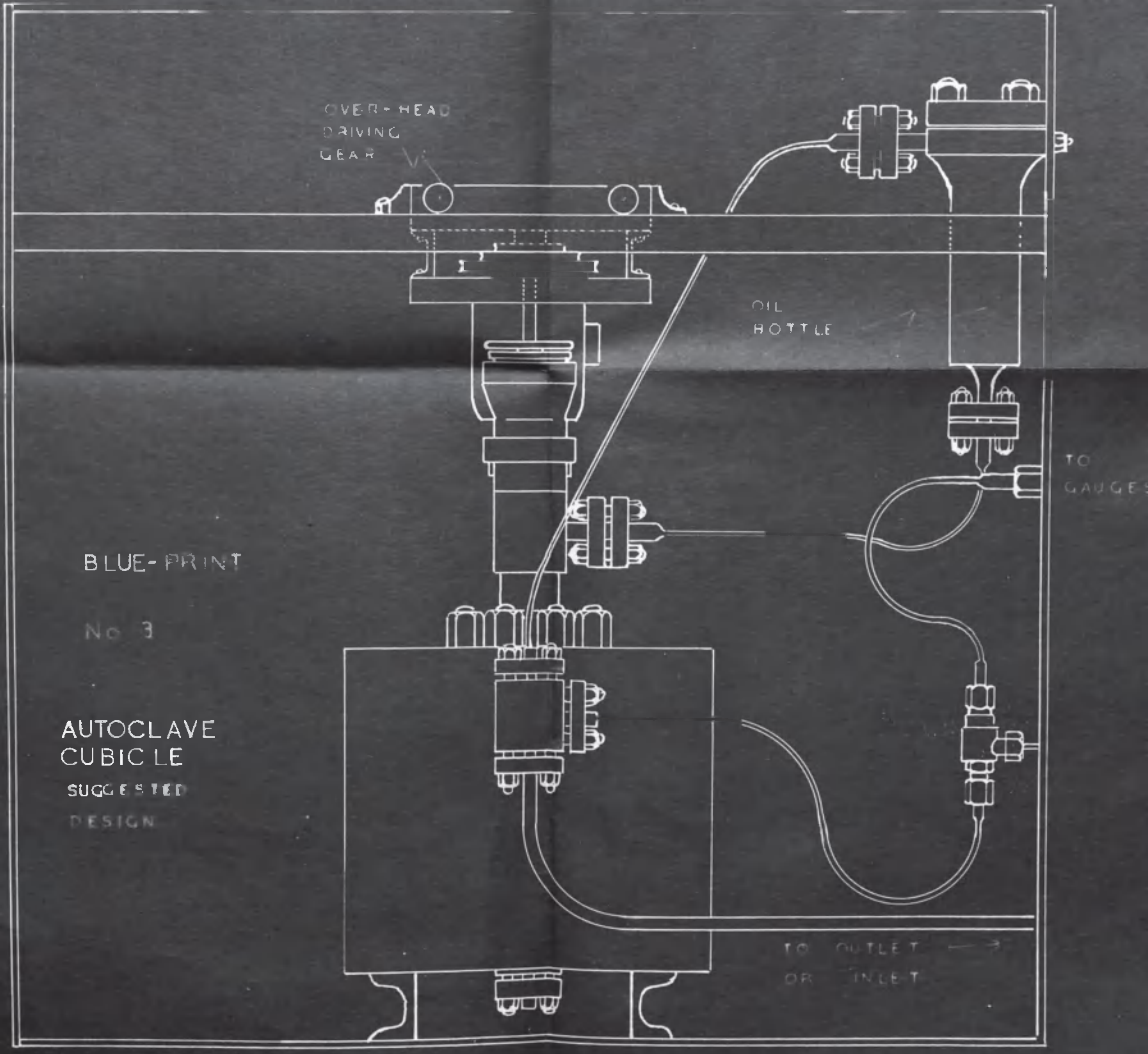
-SCALE HALF-SIZE-

BLUE-PRINT
No. 2.

AUTOCLAVE
ASSEMBLY.

SUGGESTED
DESIGN.





BLUE-PRINT

No 3

AUTOCLAVE
CUBICLE
SUGGESTED
DESIGN