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CONTENTS

THE SELECTIVE HYDROGENATION OF ACETYLENE IN ETHYLENE MADE BY THE STEAM-CRACKING PROCESS

By J. A. L. SPIERS, B.Sc., A.R.I.C.*

SUMMARY

The paper describes the catalytic hydrogenation of acetylene, $C_2H_2+H_2 \rightarrow C_2H_4$, with special reference to the use of a palladium catalyst.

The reaction is exothermic and the heat of hydrogenation is calculated as −42·89 kcal/g mol at 440°F.

Details of the process and the treatment of the palladium catalyst are described and experience in the use of this is reported.

Introduction

When ethylene is made by cracking it is always accompanied by acetylene. The amount of acetylene may be from 2000 to 10 000 p.p.m. in the final ethylene product.

It is frequently necessary to remove this acetylene before the ethylene can be further processed; this paper describes the catalytic hydrogenation of acetylene with particular reference to the use of a palladium catalyst.

Acetylene can be hydrogenated to ethylene:

$$C_2H_2+H_2 \rightarrow C_2H_4$$

$$\Delta H = -42{\cdot}89 \text{ kcal/g mol}$$

or to ethane:

$$C_2H_2+2H_2 \rightarrow C_2H_6$$

$$\Delta H = -76{\cdot}47 \text{ kcal/g mol.}$$

At the same time the hydrogenation of ethylene to ethane must be kept to a minimum:

$$C_2H_4+H_2 \rightarrow C_2H_6$$

$$\Delta H = -33{\cdot}58 \text{ kcal/g mol.}$$

All these reactions are exothermic as shown. Heats of hydrogenation are calculated for 440°F from heats of formation as given in A.P.I. Project 44.

A similar set of reactions occurs for C_3 hydrocarbons; their heats of hydrogenation at 440°F are as follows:

$$\underset{\text{Methyl acetylene}}{C_3H_4}+H_2 \rightarrow \underset{\text{Propylene}}{C_3H_6}$$

$$\Delta H = -40{\cdot}49 \text{ kcal/g mol}$$

$$\underset{\text{Methyl acetylene}}{C_3H_4}+2H_2 \rightarrow \underset{\text{Propane}}{C_3H_8}$$

$$\Delta H = -70{\cdot}90 \text{ kcal/g mol}$$

$$\underset{\text{Propylene}}{C_3H_6}+H_2 \rightarrow \underset{\text{Propane}}{C_3H_8}$$

$$\Delta H = -30{\cdot}41 \text{ kcal/g mol.}$$

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Location of Catalyst

Acetylene may be hydrogenated either before or after separation of the ethylene. Before separation, hydrogen will be present in large excess if the fractionation equipment is of the type where the cracker effluent is split into a light and a heavy fraction before separation into components. A line diagram of such a plant is shown in Fig. 1.

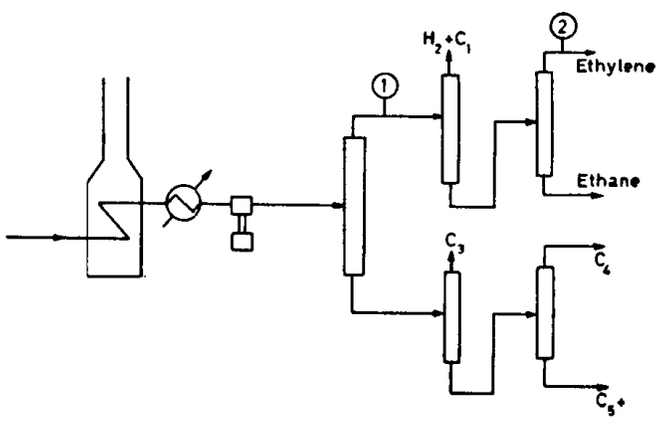

Fig. 1.—*Possible locations for acetylene hydrogenation in an ethylene plant*

A typical composition of the gases at the two locations is given in Table I.

TABLE I.—*Typical Composition at the Two Locations Shown in Fig.* 1

	Location 1 *Light Ends Gas* (*mol %*)	*Location* 2 *Ethylene* (*mol %*)
Hydrogen ...	19·0	—
Methane ...	30·0	0·25
Ethylene ...	40·0	98·5
Ethane... ...	10·0	1·0
Acetylene ...	0·1	0·25
Propylene ...	0·9	—

The advantages of acetylene removal at location 1 are:—

(1) Hydrogen is already present as a pyrolysis product.

(2) By-products of the hydrogenation will be fractionated out of the ethylene (excess hydrogen, ethane, polymer, etc.).

(3) Steam can be tolerated at this point in the process and can be used as a diluent to control the reaction if desired.

(4) If the light/heavy split is made between C_3's and C_4's, the C_2 and C_3 acetylenes can be hydrogenated together in one catalyst case.

The advantages of acetylene removal at location 2 are:—

(1) The catalyst cases are smaller because the amount of material passing is less than at location 1.

(2) The reaction can be easily controlled by the amount of hydrogen injected.

(3) Acetylene can be removed to below 5 p.p.m. consistently.

(4) Little, if any, ethylene is degraded to ethane.

(5) If desirable, the acetylene may be removed from only part of the ethylene.

(6) Some plants have no equivalent to location 1, *e.g.* hydrogen and methane are sometimes removed as the first fractionation step.

The Use of "In Situ" Hydrogen

Catalysts used for acetylene hydrogenation with "*in situ*" hydrogen are usually based on nickel, cobalt, or a combination of both. Because a large excess of hydrogen is present, the reaction is controlled by varying the inlet temperature. A temperature is chosen to give adequate acetylene removal without too much hydrogenation of ethylene. Steam is sometimes used as a reaction moderator to improve the selectivity of the catalyst. Typical operating conditions are:

Space velocity	2000–3000 standard ft³/h ft³ reactor space.
Temperature	350–500°F.
Pressure	250–350 lb/in² gauge
Ethylene loss	½–1%.
Acetylene in product	10–50 p.p.m.

The catalysts have a life between regenerations of two to eight months. Regeneration is carried out by steaming, with or without air addition. This is followed by reduction of the catalyst to the active form with hydrogen at a temperature of 700 to 800°F. A typical catalyst has an overall operating life of two to three years.

Experience with Palladium Catalyst

At one chemical works, palladium catalyst is used to hydrogenate acetylene in product ethylene. The choice of catalyst and location was made for the following reasons:

(1) The ethylene plants had a layout which precluded the use of *in situ* hydrogen.

(2) Acetylene removal was not necessary for the bulk of the ethylene.

(3) The purified ethylene was required with an acetylene content consistently less than 5 p.p.m.

After three years' experience with this catalyst, it is generally held that the choice of catalyst was a good one.

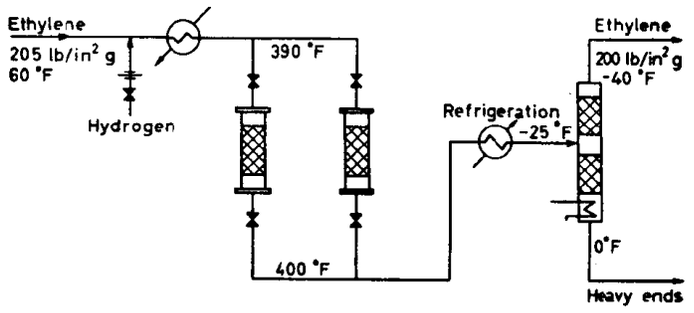

Fig. 2.—*Acetylene hydrogenation unit*

The hydrogenation unit consists of a heater, two reactors and a fractionating tower. A flow-diagram with operating conditions is shown in Fig. 2. One of the reactors is in service at any time with the other reactor on stand-by or under regeneration.

Hydrogen is added to the ethylene stream at a controlled rate, the mixture is heated to about 390°F and passed through a reactor packed with catalyst. The product is then cooled and rerun through a packed tower which removes any polymer by fractionation.

The process variables are the rate of addition of hydrogen, the temperature of the pre-heater, and the space velocity.

The unit is normally operated with two to three times the theoretical amount of hydrogen required to hydrogenate the acetylene to ethylene, at a temperature of 360–400°F, and with a space velocity of 1500-6000 vol/vol h. Normally only a slight increase of temperature is observed across the catalyst bed which indicates that the heat of reaction is roughly balanced by heat losses. Any temperature increase of greater than about 10°F would indicate that excessive hydrogenation of ethylene was taking place. That might be caused by the presence of too much hydrogen.

Hydrogen is added to the ethylene feed at a controlled rate. The amount added is small—about 1 lb/h of hydrogen for an ethylene flow of 30 tons a day—and the elimination of leaks from the piping system has proved difficult and time consuming.

Unfortunately when the system was first installed, the flow-measuring orifice was followed by a pair of drying columns with several valves and joints. Screwed connections have had to be back-welded and the orifice has been relocated downstream of the driers.

The temperature of the pre-heater is normally controlled to remain at 390°F. This temperature ensures complete hydrogenation of acetylenes, but is not high enough to cause excessive formation of polymers. It is believed that a lower temperature could be used when the catalyst is fresh but this has not been investigated because of the consequences of an acetylene breakthrough to the plant using the ethylene.

The space velocity depends on the feed rate to the unit and this can vary widely. Over the range 1500-6000 vol/vol h no difference whatever has been observed in the efficiency of hydrogenation. An increase in polymer make at lower space velocities had been anticipated but this has not been apparent in practice.

It is found that polymer is formed during hydrogenation. An ethylene feed-stream containing 3000 p.p.m. of acetylene results in an effluent containing 50-100 p.p.m. of polymer. The polymer is removed in a packed rerun column following the catalyst beds. The polymer has the properties given in Table II. Distillation data are given in Table III.

TABLE II.—*Some Properties of the Unwanted Polymer*

Bromine Number... ...	193
Specific gravity	0.71

TABLE III.—*Distillation Data*

I.B.P.	32°C
10%	40°C
50%	81°C
90%	158°C
F.B.P.	180°C

The catalyst is regenerated after about six months' operation. The need to regenerate is shown by a sporadic breakthrough of acetylene. The acetylene content of treated ethylene is monitored by bubbling the ethylene through a solution of ammoniacal cuprous sulphate containing gelatine. This solution is sensitive to acetylenes in excess of 3 or 4 p.p.m. Copper acetylide is precipitated but is peptised by the gelatine, thus giving a pink colour. The solution in the bubbler is changed every shift.

Regeneration of the catalyst is carried out by steaming at about 850°F followed by conventional steam/air decoking; no reduction step is required. An auxiliary furnace is used to supply the heat for regeneration. As this furnace is used only infrequently and its use can be planned well in advance, it can usually be shared with some other service such as regenerating a desiccant.

When a regenerated (or fresh) bed is to be put into service, the air is displaced with inert gas and the bed is heated to the operating temperature. It is then placed in parallel with the operating bed, at first with a low flow, until it is operating efficiently.

It would be desirable to carry out the regeneration at a somewhat higher temperature than is reached in practice. A temperature of 1000°F would ensure a more complete combustion of the carbon deposit. Unfortunately the temperature of regeneration is limited by the maximum allowable outlet temperature of the regeneration furnace and by heat losses from the system.

In some applications it may be possible to dispense altogether with the regeneration furnace: the catalyst would then be discarded when it became inactive. The need for regeneration equipment will be revealed by a comparison of the cost of extra equipment with the cost of increased consumption of catalyst. If a temporary interruption in hydrogenation can be tolerated, one reactor may be sufficient. This would result in a further reduction in plant cost.

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MOLYBDENA CATALYST DEACTIVATION — THE PROBLEM AND ITS SOLUTION

By L. BROUSSARD, Ph.D.,* K. E. DRAEGER, Ph.D.,* and A. B. WELTY, Ph.D.†

SUMMARY

The importance of proper catalyst pretreatment for molybdena-alumina hydroforming catalysts has been observed in both fixed-bed and fluidised-bed operations. These data show that for highest activity these catalysts must be reduced in such a way as to avoid producing crystalline molybdenum oxide; that is, molybdena which produces a characteristic X-ray diffraction pattern. Laboratory studies of the reduction indicated that the formation of crystalline molybdena increases with residence time, temperature, water partial pressure, and catalyst age. The application of these data to the design of commercial units resulted in the elimination of catalyst deactivation by crystalline molybdena.

Introduction

The fluidised molybdena hydroforming process is one of a number of catalytic reforming processes for improving the quality, particularly the octane number, of virgin and cracked naphthas. The process has been discussed in detail.[1,2,3] In catalytic reforming, the octane improvement is accomplished in several ways:

(1) by the dehydrogenation of naphthenes to aromatics,

(2) by aromatisation of paraffins,

(3) by isomerisation of paraffins, and

(4) by cracking to lighter products.

The catalyst employed in the fluidised molybdena hydroforming process is molybdena supported on alumina having a high surface area. The reactor operating conditions are generally in the range of 875–975°F and 200–300 lb/in² g with 2000–8000 standard ft³/barrel of hydrogen-rich recycle gas. The flow-diagram for a commercial unit is presented in Fig. 1.

During the reforming process the catalyst gradually becomes fouled with coke and thereby loses its activity. This fouled catalyst is reactivated by stripping with steam to remove entrained and adsorbed hydrocarbons and then circulating it to a regenerator where the coke is burned off with air at about 1100°F. During regeneration the molybdena (MoO_2) is oxidised to molybdenum trioxide (MoO_3). The regenerated catalyst is circulated back to the reactor where contact with hydrogen-rich gas reduces the trioxide to a lower oxide.

Molybdena hydroforming was originally developed as a fixed-bed process for upgrading the octane number of virgin naphtha. The first commercial unit went on stream in November, 1940. Later, the process was modified to produce nitration-grade toluene that was so urgently needed for the war effort.[4] These operations were carried out in a cyclic fixed-bed process in which a reactor was "on oil" for only about four hours before it was necessary to regenerate the catalyst with air to remove coke. In the development of the fixed-bed process it was found necessary to pretreat the regenerated catalyst with hydrogen-containing gas under very special conditions to produce an active catalyst. Elimination of the pretreatment step or carrying out pretreatment under non-optimum conditions resulted in very poor catalyst performance.

Catalyst Reduction Facilities

After the war molybdena hydroforming was further developed as a process for upgrading the octane of virgin naphtha. One of the improvements made was to convert the process from a cyclic fixed-bed process into a continuous fluidised process. In view of the critical nature of the pretreatment step in the fixed-bed process, great consideration was given to the pretreatment of the catalyst after regeneration in the fluidised unit. In initial pilot-plant studies of the fluidised process a separate pretreatment vessel was installed in the catalyst transfer line between the regenerator and the reactor. Catalyst was pretreated by injecting recycle hydrogen into this pretreatment zone. Later on, it was shown that improved catalyst activity was obtained by eliminating this separate pretreatment vessel. This is the scheme shown in Fig. 1.

One of the advantages of fluidised molybdena hydroforming over fixed-bed molybdena hydroforming is that heat liberated during catalyst regeneration can be utilised in the reaction step. This is accomplished by circulating the hot regenerated catalyst to the reactor without external cooling of the catalyst. Therefore, a satisfactory method of pretreating the catalyst must not only give high catalyst activity but must also preserve the sensible heat of the regenerated catalyst.

In developing the fluidised process, with various conditions of pretreatment, catalyst activity was sometimes quite low, showing that the method of pretreatment would also be a critical part of the fluidised process. The chemical and the normal physical properties of the low-activity catalyst did not appear any different from those of catalysts of high activity. Almost the only difference that was found was the presence of X-ray diffraction lines indicating the presence of molybdenum

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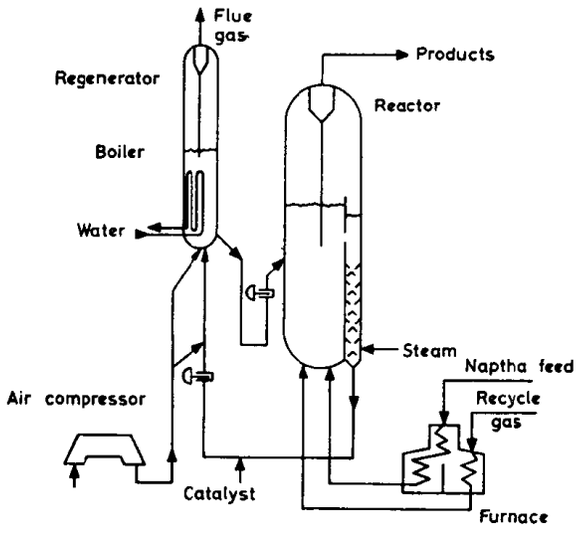


Fig. 1.—*Fluidised-bed hydroformer*

dioxide crystallites in the catalyst of low activity. Laboratory studies showed that these lines disappeared and lines representing the trioxide did not appear when the catalyst was oxidised. The crystalline dioxide lines did not reappear if the catalyst was reduced under what was later shown to be mild reduction conditions.

Under regeneration conditions, molybdenum trioxide is quite mobile on the alumina surface and is generally present in a non-crystalline form; that is, the trioxide does not produce a characteristic X-ray diffraction pattern. This mobility of molybdenum trioxide results in its redispersion during regeneration. During reduction with hydrogen-containing gas, molybdenum trioxide is converted either to a non-crystalline lower oxide or to crystalline molybdenum dioxide, depending upon reduction conditions employed. Crystalline dioxide is defined as that which produces a characteristic X-ray diffraction pattern. Sizes of crystallite dioxide of about 50 Å or larger are required before they can be detected by X-ray diffraction in this catalyst system.

It is a generally accepted fact that the activity of supported-type catalysts is influenced by the dispersion of the active component on the support of large surface area. A problem in the development of catalysts is the development of techniques for measuring the dispersion of the active component. Magnetic susceptibility methods[5] have been applied to determine the dispersion of chromia on alumina, nickel oxide on alumina and on titania, ferric oxide on alumina and on titania, copper oxide on alumina, vanadia on alumina, and nickel on silica. Hydrogen chemisorption[6] has been used to measure the dispersion of platinum on alumina. X-ray diffraction can be used in those cases where the active component is crystalline and is present in sufficient concentration.

Measurement of Crystalline Molybdena

The measurement of amount of molybdenum trioxide which had been converted to dioxide crystals was carried out with a conventional X-ray diffractometer using copper X-radiation. The molybdenum dioxide diffraction line corresponding to a *d*-spacing of 1·70 Å was measured because this line was free of interference from the diffraction pattern of the alumina support. The area (peak height times width at half-maximum) of this diffraction line was related to the amount of crystalline dioxide by calibrations involving samples of alumina dry-mixed with various amounts of crystalline dioxide prepared by careful reduction of bulk crystalline trioxide.

Effect of Crystalline Molybdena on Activity

The presence of crystalline molybdenum dioxide reduces the catalyst activity as shown in Fig. 2. Study of these data indicated that the molybdena crystals were formed during pretreatment of the catalyst. During this period the catalyst was being pretreated in a pretreatment section located in the circulating system between the regenerator and the reactor. The problem was, therefore, to find a method of pretreating and injecting catalyst into the reactor which would give high catalust activity; *i.e.*, no crystalline molybdena.

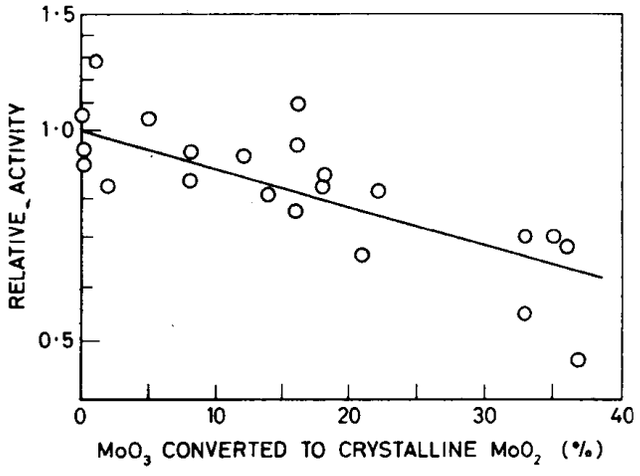


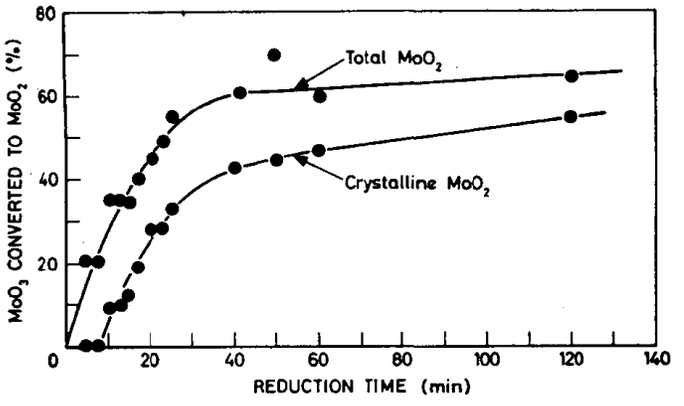
Fig. 2.—*The effect of crystalline molybdena* (MoO_2) *on activity*

Laboratory Studies on the Production of Crystalline Molybdena

It was found that crystalline molybdena could be produced in the laboratory by treating catalysts used in a pilot plant at atmospheric pressure in a fluidised bed at temperatures in excess of 800°F with hydrogen containing substantially large amounts of water. Crystalline molybdena could not be produced under similar conditions with fresh catalyst: however, artificially aging the catalyst by heating made it susceptible to the formation of crystalline molybdena. As crystalline molybdena could be produced in the laboratory, the problem of finding methods of satisfactorily pretreating the catalyst was studied in the laboratory.

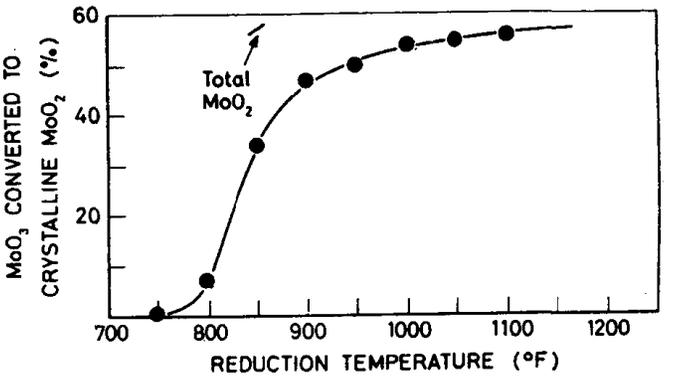
The effect of reduction time

The effect of time on the reduction of molybdenum trioxide to molybdena and on the formation of crystalline molybdena is shown in Fig. 3. The total amount of molybdena was calculated from the measured average valence (from oxygen required to convert it to the trioxide) of the reduced sample. As shown here, at 850°F the total amount of molybdena increases quite rapidly during the first 30–40 minutes and then appears to increase slowly thereafter. Crystalline molybdena presents a similar pattern, but there appears to be a short induction period before any crystalline molybdena appears.



Temperature: 850°F
Pressure: 0 lb/in²g
67 mol% water and 33 mol% hydrogen.

Fig. 3.—*The effect of reduction time on the formation of crystalline molybdena* (MoO_3)



Reduction time: 30 min
Pressure: 0 lb/in²g
67 mol% water and 33 mol% hydrogen.

Fig. 4.—*The effect of temperature on the formation of crystallin molybdena* (MoO_3)

The effect of reduction temperature

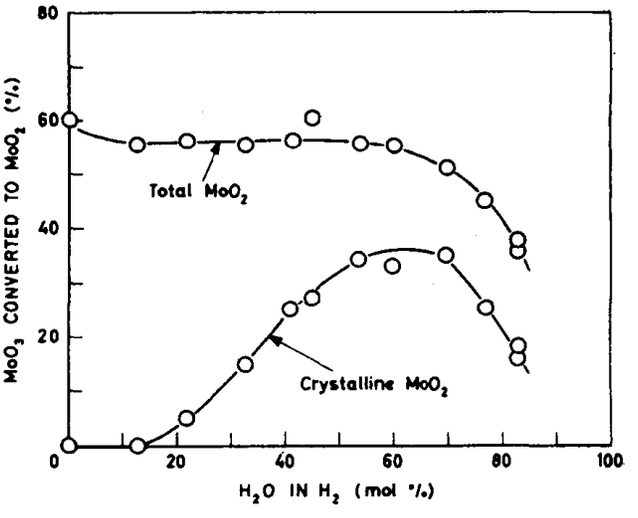
The effect of temperature on the formation of crystalline molybdena is shown in Fig. 4. The formation of crystalline molybdena increases rapidly over the range of 800–900°F.

The effect of water partial pressure

As shown in Fig. 5, increasing the water partial pressure has little effect on the reduction of molybdena until high concentrations of water, about 60 mol %, are reached. At these high concentrations the amount of trioxide reduced to dioxide decreases. The formation of crystalline molybdena is, however, greatly affected by the concentration of water and shows a maximum at 60 mol % water. Below 15% water in hydrogen, no crystalline molybdena was observed.

The effect of catalyst type and of surface area

The effect of the surface area of the catalyst on the susceptibility to form crystalline molybdena is shown in Fig. 6 for one type of alumina support. No crystalline molybdena was observed in this laboratory test for specific surface areas larger than 150 m²/g. This correlation is valid regardless of whether this catalyst is desurfaced in a pilot plant, in a commercial unit, or in the laboratory by heat treatment. For other alumina bases the curve is shifted along the abscissa of Fig. 6.



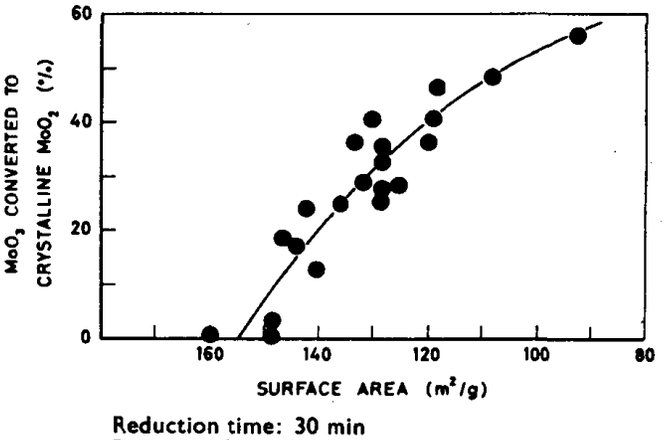
Reduction time: 30 min
Pressure: 0 lb/in²g
Temperature: 850°F.

Fig. 5.—*The effect of water partial pressure on the formation of crystalline molybdena* (MoO_3)

Interpretation of Experimental Work

In the fluidised process, carbon-containing catalyst is regenerated by burning this carbon at about 1100°F. At this temperature, the vapour pressure of molybdenum trioxide is relatively high but is still insufficient to cause significant loss of trioxide from the alumina support. However, the vapour pressure is sufficiently high to produce a two-dimensional diffusion of molybdenum trioxide over the alumina surface. Since no crystals of trioxide are ever observed by X-ray diffraction on regenerated catalysts, this diffusion of trioxide probably causes a mono-molecular layer of trioxide covering part of the surface of the alumina.

When the molybdenum trioxide is reduced to the dioxide, the latter may either remain associated with the alumina surface in a very thin layer, or the molybdenum and oxygen atoms may migrate and associate themselves in such a way as to form crystals of molybdena which can be detected by X-ray. The extent to which this occurs depends on the



Reduction time: 30 min
Pressure: 0 lb/in²g
Temperature: 850°F
67 mol% water and 33 mol% hydrogen.

Fig. 6.—*The effect of surface area on the formation of crystalline molybdena* (MoO_3)

relative cohesive forces between the molydbena and the surface of the alumina, and those within a crystal of molybdena. The effects of steam and of desurfacing can be interpreted in this light.

The energy with which alumina holds adsorbed molecules, including those of molybdena, probably is reduced by desurfacing, thus allowing more migration to form crystalline molybdena. Water is known to adsorb on alumina even at these high temperatures ; water would then be expected to compete with the molybdena for available sites on the alumina, thus also allowing more migration of the molybdena to form crystals.

The effect of temperature suggests that the cohesive forces between atoms within a crystal of molybdena relative to those between molybdena and the alumina surface increase with increasing temperature. It is also possible that the dispersed state of molybdena on alumina does not represent true equilibrium and that, because of higher solid-state reaction-rates at the higher temperatures, true equilibrium is more closely approached.

Plant Operations

These laboratory studies indicate that the formation of crystalline molybdena increases with residence time, temperature, the partial pressure of water, and the age of the catalyst. Similar trends were noted when operating a pilot plant. These results indicate that the catalyst should be pretreated at the lowest practical temperature, for shortest feasible time, and the highest possible rate of flow of gas to dilute the water of reduction. All these factors operate in the direction of carrying out the reduction at reactor conditions ; that is without separate pretreatment stage. Injection of fresh regenerated catalyst into the reactor without prior reduction was found to be quite satisfactory and this operation was incorporated into the design of commercial hydroforming units. In view of the difficulties in pretreating in the fixed-bed units, satisfactory operation of fluidised beds in the absence of a separate pretreatment stage was quite unexpected and could not have been predicted from data relating to previous fixed-bed operations.

The laboratory data shown in Fig. 6 shows an increase in susceptibility to produce crystalline molybdena as surface area of the catalyst decreases. However, reducing conditions in commercial units not having a pretreatment zone are appreciably milder than those used in the standard laboratory test. No more than a trace of crystalline molybdena was ever found in reactor catalyst from commercial units incorporating these designs even though catalyst surface areas as low as 80 m^2/g have been encountered in these units.

Acknowledgment

The authors are pleased to acknowledge the many contributions that D. R. McAdams made during the course of this study.

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DEVELOPMENT AND PERFORMANCE OF CATALYSTS FOR THE DESULPHURISATION OF PETROLEUM DISTILLATES

By F. W. B. PORTER, B.Sc., F.Inst.Pet. (ASSOCIATE MEMBER)* and E. C. HOUSAM, B.Sc.*

SUMMARY

A brief account is given of the rapid growth of catalytic processes in the petroleum industry in the last two decades. The paper also contains a detailed case study of the work necessary to develop a catalyst suitable for large scale operations, commencing with initial laboratory and pilot plant studies and extending into their performance in commercial operations.

Desulphurisation catalysts were chosen for this case study because they have been the subject of an intensive investigation by British Petroleum and while the approach was, and still is, largely empirical the underlying problems are common to many other cases of catalyst development.

Introduction

For many years the petroleum industry has depended largely upon thermal processes for changing the product-pattern of crude oils but within the last two decades the use of catalysts and catalytic processes on a world-wide basis has shown a phenomenal increase. The advent of fluidised catalytic cracking in the 1940's and catalytic reforming in the 1950's are two outstanding examples; catalytic cracking processes had expanded to treat 250 million tons per annum by 1960, and catalytic reforming has increased from about 4 million tons per annum in 1950 to about 150 million tons per annum in 1960. The increase of catalytic cracking was no doubt due in large measure to the development of the fluidisation technique which accompanied the development of suitable catalysts. However, the increase in catalytic reforming was due almost entirely to the development of the platinum-type catalyst. This increase has also provided a supply of hydrogen-rich gas which has led to a marked increase in the use of catalytic desulphurisation and other hydrofining processes, which now total about 150 million tons per annum.

The ever increasing demands for higher quality in motor gasolines, lubricating oils, fuels, speciality products, and feedstocks for the petroleum chemical industry make it more and more necessary for the petroleum industry to segregate and treat specific fractions of crude oil by the most appropriate process and there is no doubt that the use of catalytic processes will continue to expand; recent developments in the hydrocracking and isomerisation fields are a case in point. As a consequence of the development of processes using hydrogen, the demand for this gas must increase and one can also look forward to the increased development of catalytic processes for the production of hydrogen from petroleum feedstocks.

As a typical example of the development of a catalyst for the treatment of petroleum feedstocks, desulphurisation catalysts have been chosen because they have been the subject of an intensive investigation by British Petroleum Co. Ltd.; also, a later paper to be presented in this symposium will complete the picture from the catalyst manufacturer's point of view. The remainder of this introduction will give the background to this aspect.

In general, Middle East crudes have high sulphur contents although they have reasonably low wax and metallic constituents. Gas oils in particular have relatively high cetane numbers but their sulphur contents, which range from 0·6 to more than 1·0 per cent weight, depending upon the region from which the crudes are obtained, made it difficult to meet the market demand for low-sulphur high-speed diesel fuels.

Early in 1944 the British Petroleum Company realised that forward planning would demand some method of desulphurising, in the first place, the middle distillate boiling range and ultimately, heavy distillates and residual fuels. A programme of research into this field was therefore instigated to develop an economical process for the desulphurisation of petroleum products above the gasoline range. In the first place, the process was required for distillate feedstocks but it was hoped that research would permit its extension into the residual field.

Non-catalytic processes were first examined, *e.g.* solvent refining methods, but the problems of low yields and the disposal of highly sulphurous extracts were big disadvantages.

Numerous literature sources were available on the catalytic hydrogenation of petroleum fractions which showed that conversion of the sulphur compounds to hydrogen sulphide could be readily accomplished so it was decided that research in this field would be the best approach. A number of criteria were laid down at this stage as to what was most desirable in the projected process:

It had to be capable of desulphurising diesel fuel to about 0·1% weight sulphur content without degradation of yield or property.

The catalyst should be reasonably cheap, with high activity and long life between regenerations, sulphur resistant, and have adequate physical properties to withstand processing and regeneration conditions.

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The literature survey had shown that a number of catalysts were active for desulphurising light distillates and among the first to be tried were molybdenum oxide on alumina and tungsten nickel sulphides. The preliminary results showed that considerable desulphurisation was possible with diesel oil feedstocks and that the most important variables were the hydrogen partial pressure, temperature, and space velocity. Subsequently a small batch of mixed cobalt and molybdenum oxides on alumina catalyst was prepared and the increase in activity over previous catalysts was so striking that it was decided to concentrate future development work on catalysts of this type.

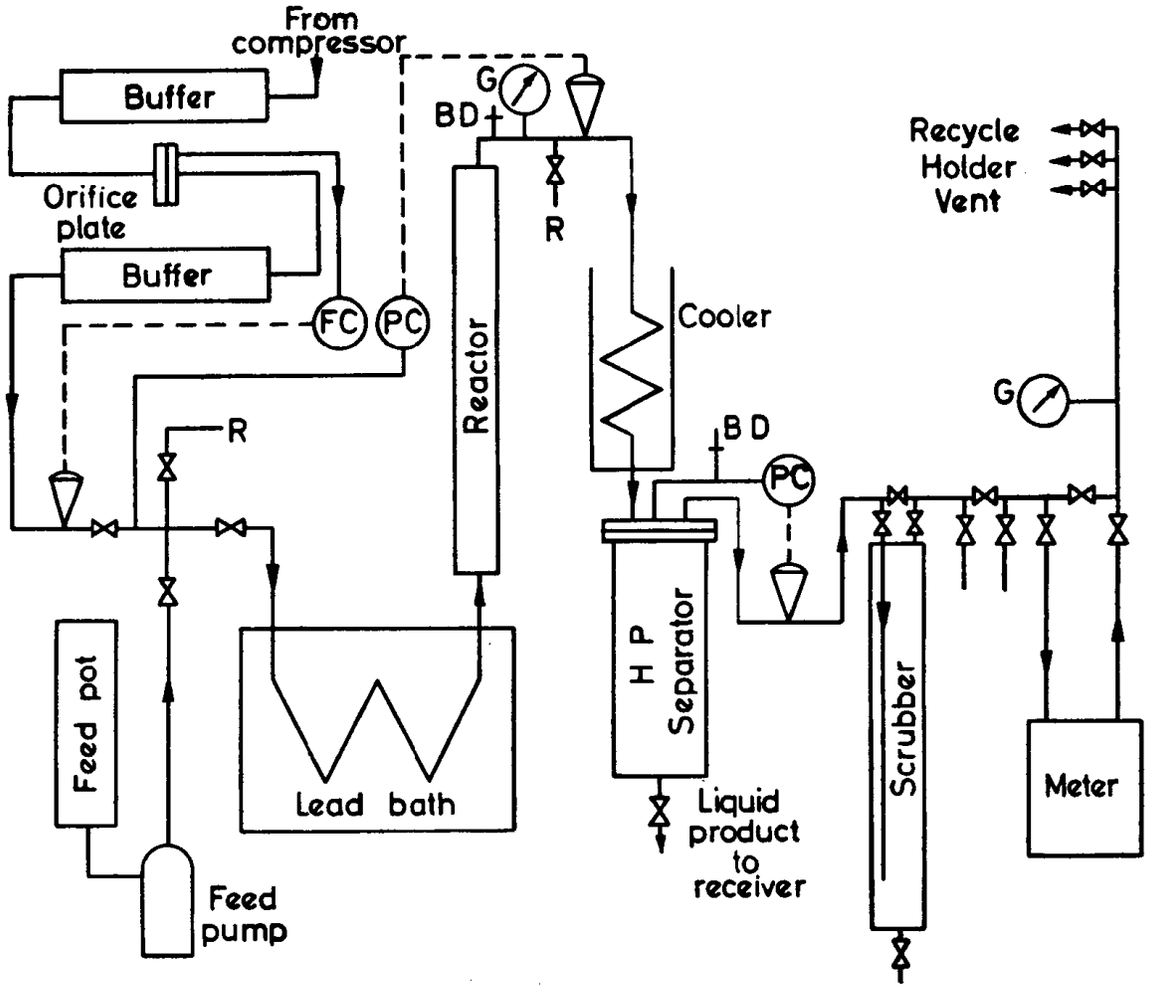
At this stage, after a survey of the effect of process variables with the cobalt and molybdenum oxide catalyst, an attempt was made to develop the theory of the process to a point where it could be employed to correlate results, predict the effect of variations in conditions, and enable the value of new catalyst formulations to be assessed rapidly. Theoretical development progressed as more experimental data were accumulated with the result that the conclusions became more precise and useful.

It was soon evident that catalyst development necessitated a rigid testing procedure, and a standard activity test, based on theoretical considerations, was formulated although later, when commercial units came into operation, it was necessary to bring the test more in line with commercial operations.

Catalyst Development

It was decided to concentrate catalyst development on the mixed cobalt and molybdenum oxides on alumina type which in the early preliminary experiments had shown far greater desulphurisation activity with feedstocks of gas oil than any other type. The first preparation was made in the laboratory by taking a mixed ammoniacal solution of ammonium molybdate and cobalt nitrate and adding it to a previously calcined (1020°F) alumina. The supernatant liquid was drained off and the impregnated alumina was dried and re-impregnated with the remainder of the solution. A final heat treatment at 1020°F was carried out after drying. The alumina used was a 4–8 mesh granular commercial material from U.S.A. consisting essentially of γ alumina.* The resulting

* *The term γ alumina is used in a generic sense to include aluminas having some water of constitution but less than one molecule of water per molecule of Al_2O_3. α alumina (see below) refers to a crystalline anhydrous alumina.*



FC = flow controller
PC = pressure controller
BD = bursting disc
R = regenerating system
G = pressure guage

Fig. 1.—*Pilot plant for catalytic desulphurisation*

catalyst had 7·2% weight MoO_3 and 4·65% CoO (the metals are expressed in this manner although it is not certain that they are actually in this form on the catalyst). A repeat preparation was made replacing the U.S.A. alumina with similar mesh-size material from Peter Spence & Sons, Ltd. and this catalyst had 6·08% MoO_3 and 3·24% CoO—a slightly lower total content of metals.

With these catalysts the process variables, *i.e.* pressure temperature, space velocity, recycle rate, and certain feedstocks were examined in small pilot plants of the type shown in Figs 1 and 2. The operation of the process consisted essentially of heating the hydrogen and feedstock to the required temperature, passing it in down flow or up flow over the catalyst bed, and then cooling and separating the reactants. The separated gases, with or without removal of hydrogen sulphide, can be recycled in the process, make-up hydrogen being added as required.

From the results obtained on the two CoMo type catalysts mentioned previously an analysis was made of the effect of the process variables and the conclusion was reached that the results could be expressed in the following form:

$$t = \frac{2{\cdot}27}{a.b.c.d.e} \cdot \log\left[\frac{98{\cdot}7}{98{\cdot}7-x}\right],$$

where:

x = amount of desulphurisation at contact time t (%).

a = coefficient which expresses the catalyst activity.

b = coefficient depending upon the composition of the reacting sulphide mixture.

c = coefficient depending upon hydrogen pressure.

d = coefficient depending upon temperature.

e = coefficient depending upon hydrocarbon partial pressure.

The contact time t is related to the space velocity, V as follows:

$$V = \frac{3{\cdot}51 \times 10^5 (P+15)}{(1000R+558)(459+T)\,t},$$

where:

V is expressed in volumes of oil per volume of catalyst per hour.

P = pressure (lb in^2 gauge).

R = gas recycle rate (10^3 standard cubic feet per barrel).*

T = temperature (°F).

For this calculation it has been assumed that the catalyst contains 50% voids and that both the recycle gas and the vapourised gas oil obey the ideal gas laws. The gas oil is assumed to have a molecular weight of 200 and a specific gravity of 0·841 giving a vapour volume per barrel of gas oil of 558 ft^3 measured at 60°F and 760 mm.

Catalysts were rated by a series of eight tests at 500 and 1000 lb/in^2 abs, space velocities of 5 and 10 v/v h, temperatures of 750 and 780°F, and gas recycle rates of 2000 and 4000 s ft^3/barrel. From the results the average value of coefficient, a, was calculated to express the relative activity of the catalyst The relative activity coefficient thus expressed is directly proportional to the space velocity employed *i.e.* doubling the activity coefficient means that twice the space velocity can be employed for the same level of desulphurisation.

* = *Cubic feet at 60°F and 760 mm Hg per 35 gallons of oil.*

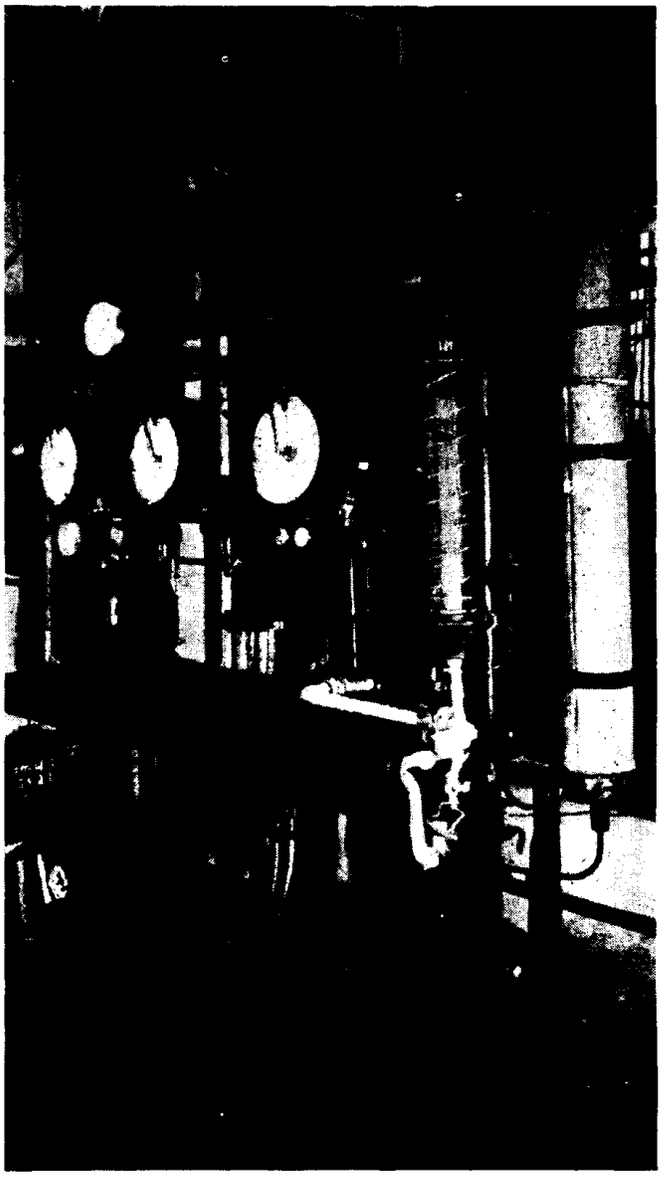


Fig. 2.—*Hydrofining pilot plant*

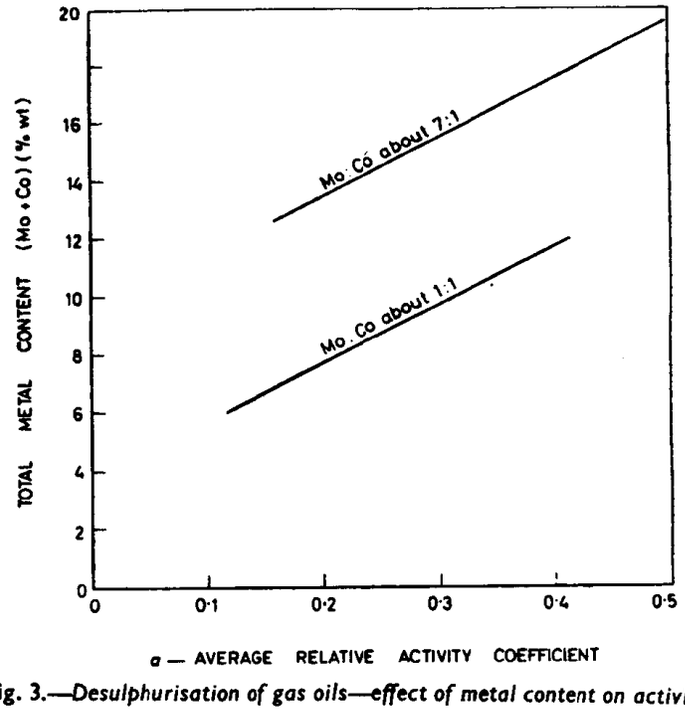


Fig. 3.—*Desulphurisation of gas oils—effect of metal content on activity*

Some 25 samples of cobalt/molybdenum catalysts were prepared and examined by this test, during which the effects of total metal content, ratio of metals, method of preparation, variations in base, sodium content of base, and final heat treatment were assessed. Fig. 3 gives an overall picture of the effect of metal content and metal ratio on desulphurising activity.

The effect of sodium content of the catalyst was examined because of prior knowledge that in dehydrogenation catalysts it was beneficial to have as low a sodium content as practicable. Experiments with the cobalt/molybdenum type catalyst showed that the effect on activity of reducing the sodium from 0·4% to about 0·1% weight was equivalent to increasing the metals content by 30%.

Preliminary experiments on the effect of final heat treatment were anomalous in that in some cases an increased activity was obtained by increasing the calcination temperature from 1020°F to 1300°F whereas in other cases a reduction in activity occurred.

One of the most important factors in choosing a suitable catalyst is the retention of activity during processing periods. Loss of activity can come from a number of causes:—

(1) Poisoning of catalyst either permanently or temporarily.

(2) Degradation of physical properties.

(3) Deposition of extraneous matter clogging the catalyst, *e.g.* carry forward of corrosion products from heaters etc.

Causes (2) and (3) can usually be cured by proper choice of initial physical properties and materials of construction but cause (1) can be much more troublesome. Under cause (1) is included what is usually the commonest cause of loss of activity, the deposit of carbon or carbonaceous material on the catalyst. While this effect is often only temporary in that the activity can be restored by regeneration, it can in some cases seriously affect the whole economics of a process. Fortunately, in catalytic desulphurisation this carbon deposition can be delayed or prevented to a large extent by the use of the partial pressure of hydogen and as desulphurisation is increased with increasing hydrogen pressure the problem can be overcome. So much so, that by proper choice of conditions with clean feedstocks, the life of the catalyst between regeneration is generally determined by demands other than loss of activity. Fortunately, also cobalt/molybdenum type catalysts on alumina bases can be readily regenerated by a burn-off technique without subsequent loss of activity.

Concurrently with the programme on the catalyst variable a very comprehensive survey of process variables and feedstocks was carried out which culminated in a full-scale design of a plant for desulphurising gas oil feedstocks, later to be installed at BP Refinery, Kwinana, Western Australia some ten years after the research work had begun. The delay came for two reasons:—

(1) Market requirements at that time for low-sulphur diesel fuels could be met by crude segregation.

(2) A hydrogen consuming process, such as had been developed, necessitated an external source of hydrogen since at that time (prior to 1950) catalytic reforming with its consequent supply of hydrogen off gas was not available.

The development of the catalyst had not gone beyond the laboratory stage before it was shown that the economics were not favourable for the immediate development of the hydrogen-consuming route. However, research at BP had by this time shown that there were possibilities in a process where the hydrogen required for the conversion of the sulphur to

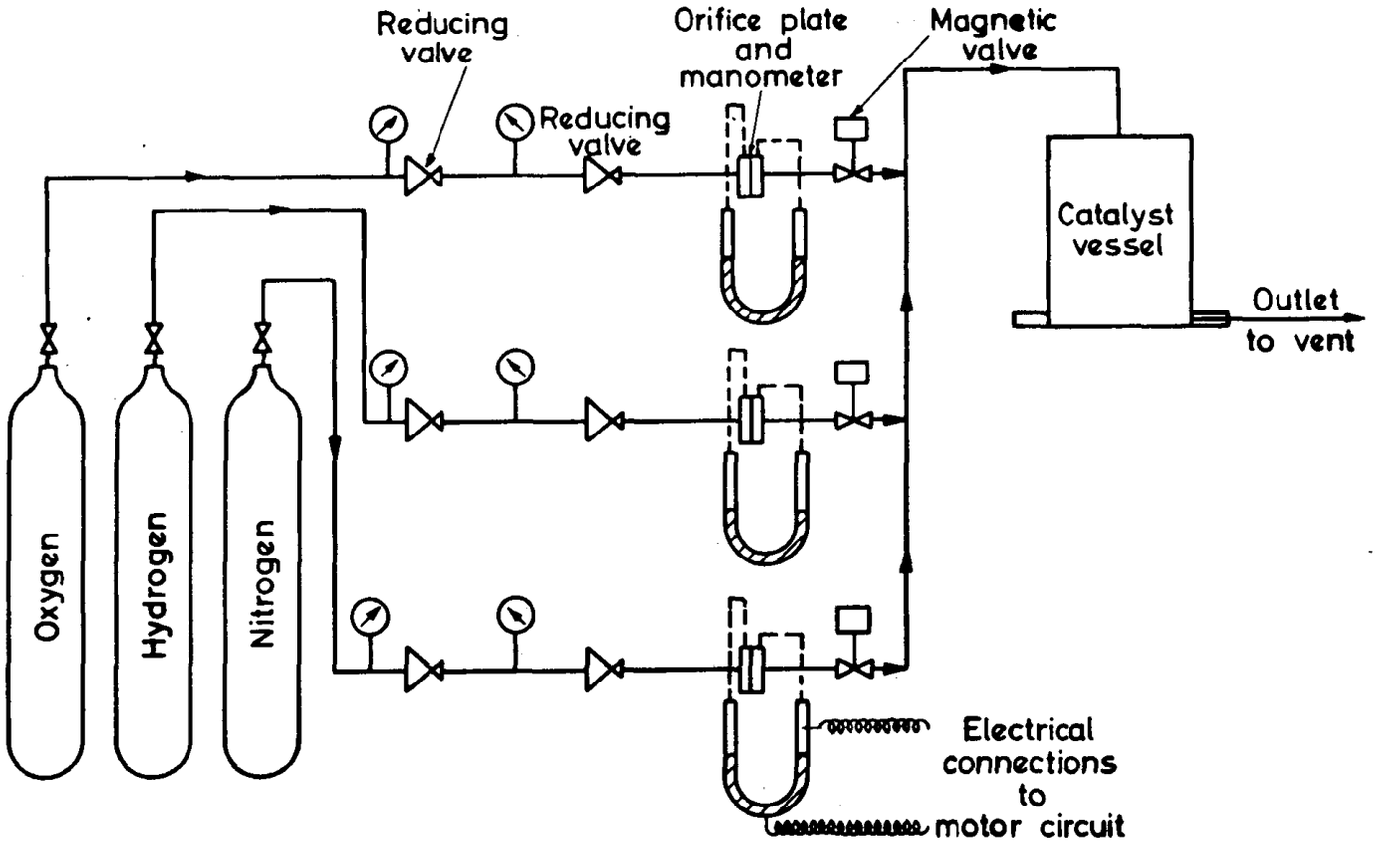


Fig. 4.—*Catalyst stability—flow diagram of test unit*

hydrogen sulphide could be supplied by partial dehydrogenation of the feedstock itself and it was in this connection that the next stage of the development of the cobalt/molybdenum type catalyst took place. The development of the process (Autofining) has been fully described[1,2,3] and the only pertinent facts required in this paper are that the process in general operated at a lower hydrogen pressure and higher temperature than does the hydrofining process. These conditions accentuate the problem of carbon laydown, consequently more frequent regeneration was required and the properties of the catalyst had to be suitably adjusted.

Experiments on catalyst composition under the new process conditions showed that, contrary to previous experience in hydrofining, a total metal content above about 15% weight had little effect on activity. It was therefore decided to standardise all future work on a catalyst consisting of about 15% MoO_3 and 2·5% CoO on a γ type alumina, a composition which had given very satisfactory results in the initial laboratory studies.

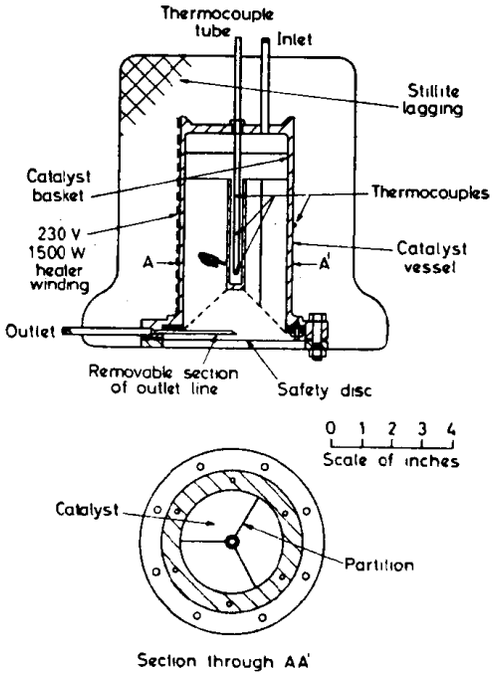


Fig. 5.—*Catalyst stability—catalyst vessel assembly of test unit*

As the construction of a large pilot plant and full-scale plant were under active consideration it became necessary to decide on such physical characteristics of the catalyst as size and form, crushing strength, and resistance to attrition. At this early stage a commercial-type molybdenum-oxide-on-alumina catalyst which had been used for catalytic reforming in U.S.A. was taken as a guide. This material was in the form of 2–4 mesh granules which would give a pressure drop, within the reactor, of the order considered to be desirable. The activity of the catalysts was assessed from the results of a standard test which compared the degree of desulphurisation obtained with a given feedstock under set conditions over a period of operation of 50 hours. The laboratory-prepared sample of catalyst was given an arbitrary rating of 100 on this test. At this stage contact was made with Peter Spence & Sons, Ltd. and joint development work then proceeded to produce material to the required chemical and physical specification. The specification laid down at this time was as follows:

CoO:	2·5–3·0% wt
MoO_3:	14–15% wt
Crushing strength:	65–75% wt retained on 5 BSS mesh
Attrition test:	65–90% wt retained on 5 BSS mesh
Activity rating:	90
Form:	2–4 mesh granular

An outline of the crushing and attrition tests is given in the Appendix. No definite values were placed on density, surface area or pore volume although it was thought desirable to have a high surface area and low density. In general chemical impurities, particiularly sodium, were to be as low as possible.

The specifications for crushing strength and attrition were based on the result of tests on the large pilot plant which by this time was in operation at the BP Grangemouth Refinery. The lower limits were equivalent to the properties of a catalyst prepared in a large scale laboratory preparation at Sunbury and subsequently used on the 100 barrels per day* pilot plant.

Finally, a commercial large batch was prepared by Peter Spence & Sons Ltd., which also proved satisfactory in the pilot plant. This catalyst had the following properties:

CoO:	2·8% wt
MoO_3:	13·8% wt
Crushing strength:	74·6% wt retained on 5 B.S.S. mesh
Attrition test:	82·3% wt retained on 5 B.S.S. mesh
Bulk density:	0·708 g/cm^3
Activity rating:	95
Form:	2–4 mesh granular

Concurrently with the investigations into the commercial manufacture of a catalyst with suitable physical properties and activity, the effect of regeneration had to be investigated. As mentioned previously, the deposit of carbonaceous matter on a catalyst progressively decreases the activity and a stage is ultimately reached when the catalyst has to be reactivated; the interval depended upon the feedstock being processed.[2] Early experimental work had shown that laboratory samples could be reactivated completely by a simple burn-off technique but no information was available as to the effect of repeated regeneration on the physical properties and activity of the catalyst.

Consequently an apparatus was designed (Figs 4 and 5) in which it was possible to subject catalysts (in batches of three) to repeated cycles of oxidation and reduction with oxygen and hydrogen respectively. Each step was of 20 minutes duration with a nitrogen purge between and could be carried out at temperatures up to 1200°F at atmospheric pressure. After a predetermined number of cycles (about 720) the catalyst sample was removed and its activity and physical properties were compared with those of the fresh sample. In this way by assuming that a catalyst would have a life of, say, two years with 24 regenerations, it was possible to predict that the physical and other properties were satisfactory.

Although initial laboratory regenerations were carried out by burn-off of carbonaceous matter using a mixture of nitrogen and air, it was intended to use steam and air in practice. Consequently investigations into the effect of steam on the catalyst had to be carried out. From this work rigid conditions could be laid down for satisfactory reactivation, in particular

* *One barrel contains approximately* 35 *imperial gallons.*

the oxygen concentration, the maximum allowable temperature, and the steam pressure. The latter two were also of importance due to the volatilisation of molybdenum oxide at high temperature and high partial pressures of steam.

The rate of loss of molybdenum from the catalyst was first studied by passing mixtures of nitrogen and air over the catalyst at a space velocity of 900 v/v h in the temperature range 1000°F to 1400°F. The results showed the reaction to be of first order with respect to molybdenum, and that the effect of temperature can be expressed by an equation of the Arrhenius type, which for atmospheric pressure operation and a space velocity of 900 v/v h at standard temperature and pressure is shown to be:

$$\log_{10} K_0 = \log_{10}\left(\frac{2{\cdot}303}{t}\log_{10}\frac{a}{b}\right)$$

$$= 4{\cdot}16 - \frac{13390}{T},$$

where:

K_0 = velocity constant (zero steam partial pressure).

a = initial molybdenum concentration.

b = final molybdenum concentration after t hours.

T = the temperature (°R).

When steam is introduced into the system the reaction is still of first order but has become more sensitive to temperature as shown by the equation:

$$\log_{10} K_{15} = \log_{10}\left(\frac{2{\cdot}303}{t}\log_{10}\frac{a}{b}\right)$$

$$= 8{\cdot}84 - \frac{19710}{T}.$$

K_{15} is the velocity constant at a steam partial pressure of 15 lb/in² abs and the other symbols have the same significance as previously.

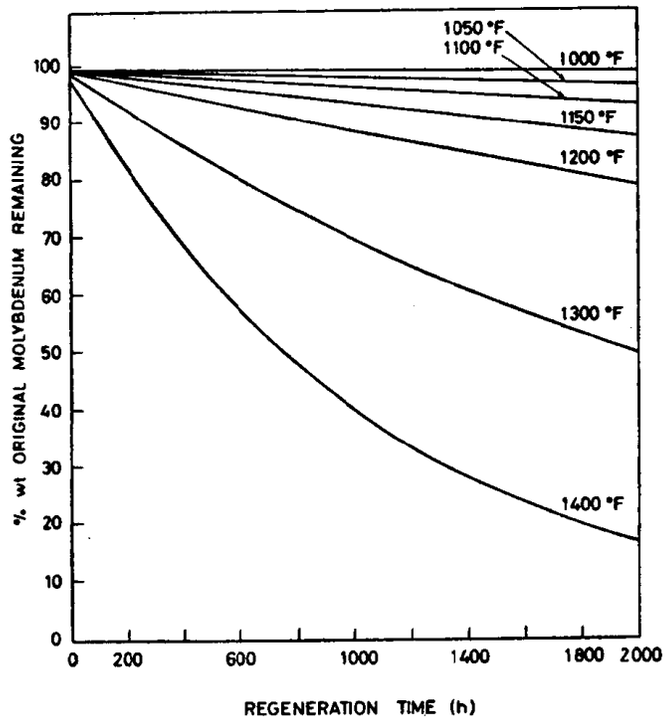


Fig. 6.—*Loss of molybdenum—effect of temperature with 5% air in inert gas regeneration at atmospheric pressure*

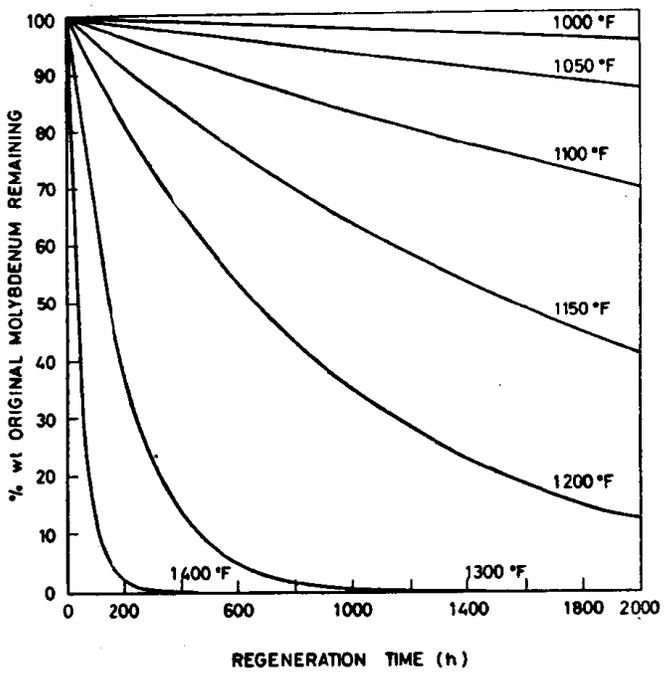


Fig. 7.—*Loss of molybdenum—effect of temperature with 5% air in steam regeneration (steam partial pressure = 15 lb/in² abs)*

The constants for these equations were derived from work on a carbon-free oxidised catalyst which means that the equations will predict higher rates of loss than would be obtained in practice.

As shown in Fig. 6, the loss of molybdenum from the catalyst will be less than 15% at temperatures at or below 1150°F after 2000 hours under regeneration conditions. This is equivalent to about 100 separate regenerations of 20 hours duration. The use of steam at atmospheric pressure leads to a similar loss at 1050°F (Fig. 7) while at a steam pressure of 30 lb/in² abs the same rate of loss is reached at 1000°F (Fig. 8).

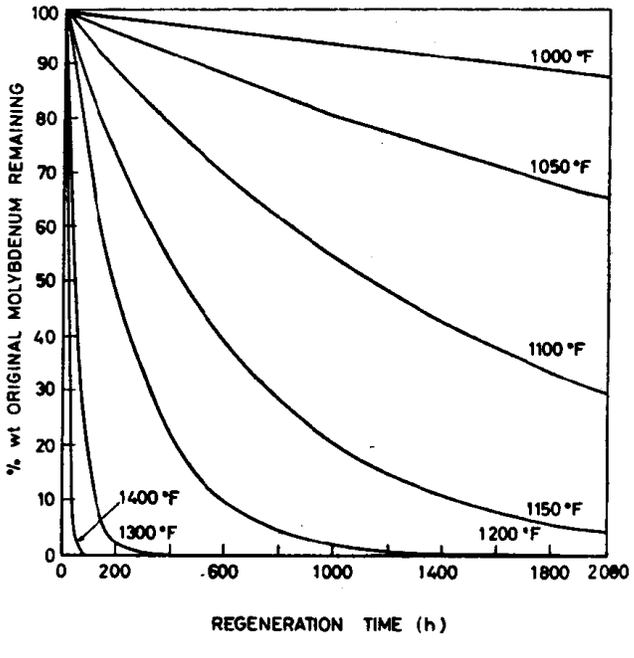


Fig. 8.—*Loss of molybdenum—effect of temperature with 5% air in steam regeneration (steam partial pressure = 30 lb/in² abs)*

No loss of cobalt from the catalysts was detected (within experimental error) and none would be expected from the known properties of cobalt oxide.

It was noticed that the crystal size of the alumina became larger after treatment at high temperatures, slight changes being apparent even at 1000°F. It was not demonstrated that this change causes any decline in activity. No formation of α alumina was detected over the whole of the temperature range examined.

Up to this stage the development work had concentrated on a catalyst suitable for the large scale unit which was in an advanced stage of design. Commercial batches of similar catalyst (2–4 mesh granular) were satisfactorily manufactured and subsequently proved adequate in commercial operations at Llandarcy Refinery. With the problem of the catalyst for the first commercial unit satisfactorily solved, more time could now be devoted to the properties of the catalyst itself. This work had two objectives:

(1) To produce catalysts of higher activity.

(2) To examine the effect of physical properties both on the activity and on the economics of the process.

An account has already been given which summarises the work on the development of a highly active fluorine promoted cobalt/molybdenum type catalyst[4] and it is proposed to concentrate on the second objective in the present paper.

The use of pelletted catalyst

In the manufacture of granulated catalyst a considerable amount of fines are inevitably produced and while reincorporation could be employed the use of pelletted catalysts was thought to be better. Consequently a number of preparations were made by the manufacturer and tests showed that the activity could be maintained. Furthermore, satisfactory physical characteristics were obtained, particularly heat stability.

A series of catalyst pellets was then examined ranging from $\frac{1}{8}$in. × $\frac{1}{8}$in. to $\frac{3}{8}$in. × $\frac{3}{8}$in. and it was shown that activity increased with decrease in paricle size although pressure drop simultaneously increased. An economic balance has therefore to be reached taking into account the cost of pellets, the volume of the reactor, and the costs of the compressor before a choice can be made of the most economical size. Investigations showed $\frac{1}{4}$in. × $\frac{1}{4}$in. pellets to be satisfactory and subsequently these pellets were charged to the large-scale pilot plant at Grangemouth for longer-term testing.

By this time the 3500 bpd* Autofining unit was about to be commissioned at Llandarcy Refinery and a similar unit was under construction at the Aden Refinery, both for the desulphurisation of tractor vaporising oils. The Llandarcy unit used the 2–4 mesh granular catalyst while the results of the catalyst development work enabled a charge of $\frac{5}{16}$ in. pellets to be employed at Aden. The pilot plant at Grangemouth was also enlarged to a 500 bpd commercial operation. Details of the performance of these catalysts will be contained in a later section of this paper.

Catalytic reforming, with its associated large volumes of hydrogen off-gases, had by now been installed in various BP refineries. The forward development programme had therefore been turned again to the use of this off-gas for the desulphurisation of diesel fuels by the hydrofining route. As the development of the cobalt/molybdenum type catalyst had reached the stage where a commercial product was available for Autofining, the renewed hydrofining studies commenced with

* *Barrels per day.*

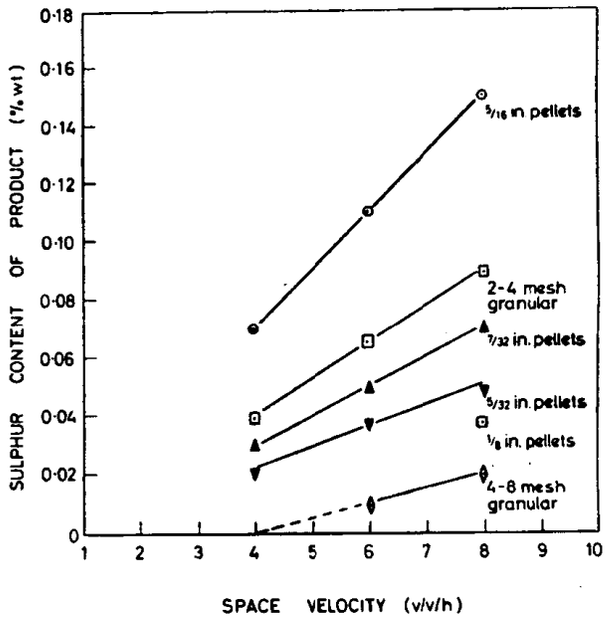


Fig. 9.—*Effect of particle size on hydrofining activity of cobalt/molybdenum catalysts*

pelletted material. Under a standard set of hydrofining conditions pellets of $\frac{5}{32}$ in., $\frac{7}{32}$ in., and $\frac{5}{16}$ in., were compared with 4–8 and 2–4 mesh granular material. The results showed that the activity for desulphurisation increased with reduction in particle size (see Fig. 9) and was directly proportional to the superficial surface area per unit volume of catalyst bed (see Fig. 10).

Experiments on the density of pellets showed that a reduction in density had a beneficial effect, apart from the economic one of reduced weight in a given sized reactor, and that the reduction could be obtained without undue sacrifice of such other physical properties as crushing strength and resistance to attrition. The general conclusion drawn from this

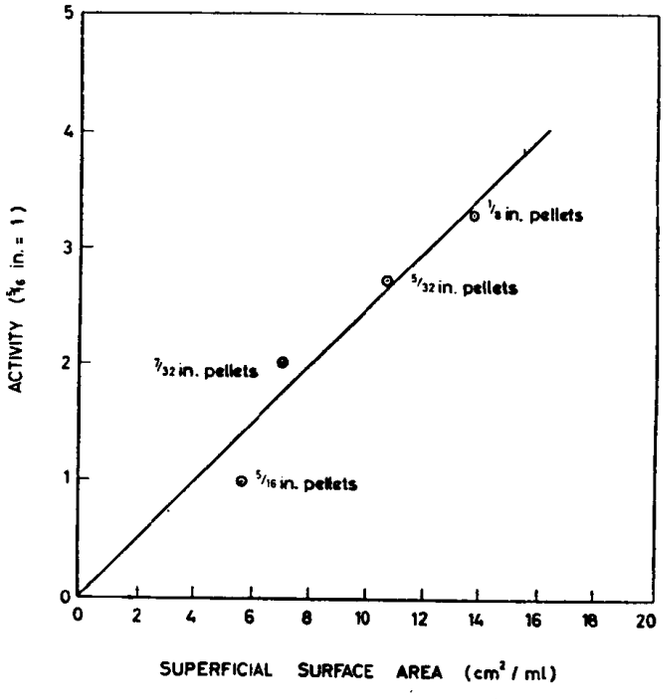


Fig. 10.—*Effect of superficial surface area on hydrofining activity of cobalt/molybdenum alumina catalysts*