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EQUIPMENT FOR GAS-LIQUID REACTIONS

BY

DONALD B. KEYES

CIRCULAR No. 19

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EQUIPMENT FOR GAS-LIQUID REACTIONS

I. Introduction

1. *Introductory.*—Gas-liquid reactions are extremely important in a great many different industries. The hydrogenation of cottonseed oil in the presence of a nickel catalyst is an excellent example. A future development which should be of extreme importance to all organic industries is the partial oxidation of organic liquids using air as the oxidizing agent. At the present time there are a few partial oxidations of commercial importance. These oxidations, however, take place in the vapor phase, the reason being that the catalyst used is unable to operate at low temperatures, and no satisfactory equipment has been designed to produce the requisite surface of contact between the two reacting phases. The carrying out of catalytic partial oxidations in the vapor phase is often disastrous because there is no adequate method of controlling the temperature of the catalyst between narrow limits. If it were possible to control the temperature within the narrow limits required, then it would be possible to operate a great many partial oxidations which have hitherto remained undeveloped. This would mean the production of a great many of our modern industrial solvents and synthetic textiles by direct action of air upon some cheap and plentiful raw material, such as the hydrocarbons. Liquids with a higher heating capacity per unit volume would exert a very beneficial effect on the temperature control if they were present as one of the reacting substances. This would be accentuated if the catalyst used were soluble in the liquid. Therefore, the great importance of satisfactory equipment for use in gas-liquid reactions can easily be seen.

There has been very little attempt to develop satisfactory equipment in which these reactions can be carried out. There is one great difficulty: A satisfactory machine should give an intimate contact between the gas and the liquid. In other words, the surface of contact between the gas and the liquid should be as large as possible. This is especially true when the gas is practically insoluble in the liquid. If the gas is fairly soluble in the liquid it is only necessary to expose sufficient surface to permit the liquid to dissolve the gas. The reaction will then take place in the liquid solution. In this case the reaction surface may be considered to be infinite.

Equipment which is normally used for absorption of a gas in a liquid or a fractionation of a liquid mixture will usually prove quite satisfactory for those gas-liquid reactions in which the gas is soluble in the liquid. On the other hand, the present commercial equipment has proved more or less unsatisfactory for those reactions in which the gas is practically insoluble in the liquid.

It is our purpose to review briefly the various types of existing equipment which have been or might be satisfactory for gas-liquid reactions, and also to report on the development of a new type of small laboratory equipment which has certain distinct advantages over equipment previously used.

2. *Acknowledgments.*—The author wishes to acknowledge the assistance rendered by MR. F. B. HOBART, formerly on the staff at the University of Illinois. He especially wants to acknowledge the very great assistance of MR. E. P. KING, graduate student at the University of Illinois. Mr. King took charge of the laboratory try-outs of the various machines mentioned in this circular.

The investigation has been carried on as a part of the work of the Engineering Experiment Station, of which DEAN M. S. KETCHUM is the director, and is one of the researches in Chemical Engineering.

II. COLUMNS

3. *Simple Spray Columns.*—It has been common practice for a great many years to absorb gases and liquids by passing the gas up a column in which a liquid is raining down in the form of a fine spray from a sprinkler or other spraying device at the top. Evaporation is often brought about in the same type of apparatus. In recent years it has been customary to use this equipment for simple reactions such as the formation of ammonium sulphate by the reaction of ammonia gas with dilute sulphuric acid.

4. *Filled Columns.*—It will be noticed that in this equipment the chances of all the gas coming in contact with the liquid while passing through a few feet of column are very small. In order to remedy this condition and obtain more surface of contact between gas and liquid, the columns have been filled with various materials. Examples of filling materials are sticks of wood laid crosswise, charcoal, short pieces of glass tubing, and special filling material in the form of short spirals inside of a small cylinder. A great deal of work has been done on the preparation of proper filling material to get the maximum contact be-

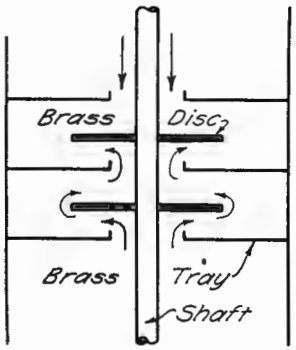

FIG. 1. WHIRLING SPRAY COLUMN

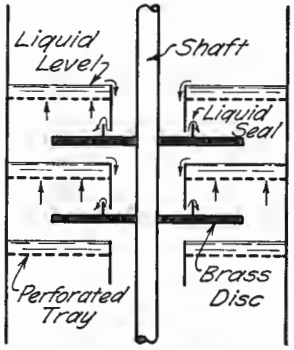

FIG. 2. IMPROVED TYPE OF WHIRLING SPRAY COLUMN

tween the gas and the liquid. In many respects this filled column is preferable to the unfilled column. On the other hand, it is not as satisfactory as the devices used in regular fractionating columns.

5. *Whirling Spray Columns.*—The Feld Scrubber (manufactured by The Bartlett Haywood Company, Baltimore, Maryland) is another satisfactory spray column. The liquid entering at the top is broken up into a fine spray by mechanically revolved baffles attached to a central vertical shaft operated by a motor on the top of the scrubber. The gas enters at the bottom and travels upward through the spray. In order to try out in the laboratory equipment which resembled the Feld Scrubber, a small column was designed as shown in Fig. 1. Fastened to the center shaft were brass disks. Fastened to the cylindrical glass side were brass trays, arranged with respect to these disks as shown. The liquid was put in at the top and the gas at the bottom. The shaft was revolved by means of a small electric motor mounted at the top. The liquid fell over the rim of the tray, dropped on to the revolving disk below, and was thrown out in the form of a spray to the walls, whence it dropped down to the next tray and then over the rim of that tray to the revolving disk immediately below. The gas passed up around the shaft coming in contact with the liquid and then over the tray, still in contact with the liquid, and finally through the spray coming off of the revolving disk. Preliminary experiments with this machine showed that it had excellent possibilities.

An improved type is shown in Fig. 2. In this case the trays are perforated, permitting the gas to pass up through the liquid instead of around the shaft—thus giving better contact with the liquid. The

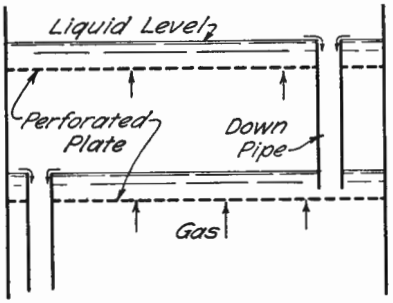

FIG. 3. PERFORATED PLATE COLUMN

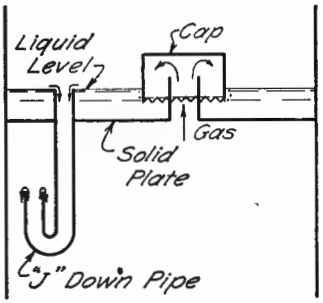

FIG. 4. BUBBLE CAP PLATE COLUMN

liquid comes down from the tray inside of a pipe which encloses the revolving shaft and then out on to the disk through a liquid seal. In other respects, this machine is similar to the one previously described.

6. *Perforated Plate Column.*—For the fractionation of organic liquids, there are two types of columns commonly used with a great many modifications. The first is the so-called perforated plate column, a section of which is shown in Fig. 3. The column is round, and every foot or so has a perforated plate which extends entirely across its cross-section. This perforated plate holds a certain amount of liquid on the top due to the fact that the gas coming up from below constantly passes through the small perforations and prevents the liquid from draining off the plate. However, when the liquid gets to the height of the edge of the down pipe, it passes down to the plate below, beneath the surface of the liquid on the lower plate. This liquid seal prevents the passage of gas up the down pipe. The plate below is of exactly the same construction except that the down pipe is on the opposite side. The liquid enters at the top of the column and passes out at the bottom; the gas enters at the bottom and passes out at the top. In other words, there is a counter current flow. The gas not only comes in contact with the liquid as it passes in the form of small bubbles up through the perforations and then through the body of the liquid, but it also comes in contact above the liquid surface where the spray from the liquid in the form of small droplets passes up and down through the gas. This type of column usually gives considerably more surface of contact than either the filled column or the spray column.

7. *Bubble Cap Plate Column.*—The best type of column yet designed for fractionation purposes is the so-called bubble cap column, a section of which is illustrated in Fig. 4. This column has not only

been used for fractionation purposes, but actual gas-liquid reactions of various kinds have been satisfactorily operated by means of it.*

This type of column has a solid plate with short tubes which permit the gas to pass upward from the plate below and collect on the underneath side of a tooth-edged cap. The liquid seal is maintained as before by a down pipe extending up from the surface of the plate. In Fig. 4 a "j" down pipe is used. This pipe is not sealed off by the liquid on the plate below, but carries its own liquid seal, due to its shape. When the gas pressure is sufficient, it forces the liquid level down to the point where small bubbles are allowed to escape at the top of the V-shaped grooves in the cap. If the pressure is considerably greater, the gas will come out in the form of larger and larger bubbles from the edge of the cap. This particular design of plate seems to furnish the greatest surface of contact between gas and liquid of any plate designed. It has the additional feature that the liquid lying on the plates is not dumped through to the bottom of the column, but remains in position in case the gas pressure should be suddenly reduced.

III. High-Speed Stirrers

8. *High-Speed Disk Stirrer.*—Churning devices have been utilized to mix a gas and a liquid into a froth in order to get contact between the two phases. A very interesting device, however, was developed some years ago for the mixing of a gas and a liquid in order to get a large surface of contact without violent motion of the liquid.† This machine consists of two round disks on the end of a shaft which revolve at between ten and twenty thousand revolutions per minute. A sketch of this machine is given in Fig. 5. These two concave circular disks are screwed together so that the edges do not quite touch, but allow a clearance between them of a few thousandths of an inch. The gas is brought down through a tube as indicated in the sketch, and allowed to bubble up through the opening in the lower disk. The centrifugal action tends not only to suck in the gas, but also to draw in the liquid and pass the two out together through the periphery. It is not known exactly how the contact is produced, but it is believed that the liquid exerts a shearing action on the gas bubbles as they escape through the periphery and breaks these up into extremely fine units. Baffles are necessary to prevent the entire mass of liquid from

*Development work done by the Research Department of the U. S. Industrial Alcohol Company.

†This high-speed stirrer was developed by the Research Department of the U. S. Industrial Alcohol Company, and is now being manufactured by the Onsrud Machine Works, Chicago, Ill.

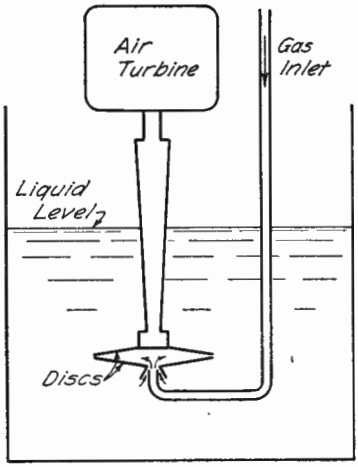

FIG. 5. HIGH-SPEED DISK STIRRER

obtaining a swirling motion and climbing up the sides of the vessel. In spite of the fact that the two disks are two circles with well polished surfaces, there is, nevertheless, considerable friction due to the very high speed of rotation.

The only real difficulty in the development of this machine was to find the proper means of turning the stirrer at the required rate, twenty thousand revolutions per minute. A small air turbine was finally decided upon, which proved to be very satisfactory. This machine was used for several gas-liquid reactions, one of the most interesting of which was the well-known reactions between ethylene gas and benzol in the presence of aluminum chloride as catalyst, to produce the various ethyl benzols. It was found that as much hexaethyl benzene could be obtained in one-half hour by the use of this machine as had been obtained formerly with the ordinary laboratory bubbling apparatus in two days.

It is quite possible that this machine could be improved upon by forcing the gas through the shaft by means of a pump instead of relying on centrifugal force. In this case the opening in the lower disk would be closed, the shaft would be hollow, and a small hole be made in the shaft above the liquid line surrounded by a collar, the collar to have a groove all around it with an opening to a pipe line from the pump. In this way, gas would be forced down the center of the shaft and out through the periphery between the two disks. This scheme would undoubtedly give greater contact between the gas and the liquid, or at least increase the capacity of the apparatus.

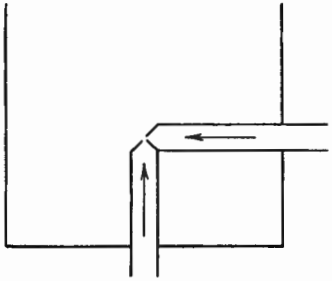

FIG. 6. RIGHT-ANGLE TUBE SLIT

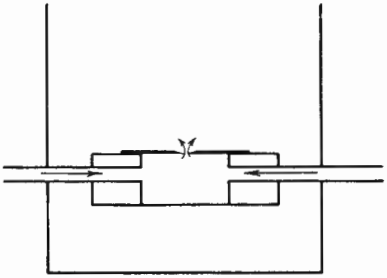

FIG. 7. SIMPLE SLIT

IV. STATIONARY SLITS

9. *Right-Angle Tube.*—One of the difficulties of the high-speed stirrer is the speed feature. It was thought possible to develop a stationary slit that would act in the same manner. Figure 6 shows the first one developed, which consisted of two tubes joined together at right angles. In one, the gas was under pressure and in the other the liquid. The narrow openings in the end were close to one another and at right angles. This caused a fine spray of liquid when the machine was operated in the gas phase or a fine spray of gas bubbles when the machine was operated in the liquid phase.

10. *Simple Slit.*—Figure 7 shows still another design in which there is a tube flattened in the middle with a very fine slit in the center of its upper side. In order to keep the edges of this slit from wearing badly due to erosion, two razor blades are fixed in position on a copper or brass block. The gas is sent in one side and the liquid in another. This is usually operated in an outside gaseous phase. Both the gas and the liquid can be heated before they come in contact with one another, and the whole apparatus can be operated in a thermostat if desired. The results using this apparatus were very satisfactory, for example, the ethylene benzol reaction was tried and the results compared very favorably with those obtained by means of the high-speed stirrer previously mentioned.

11. *Elongated Slits.*—It is conceivable in certain catalytic reactions that the catalyst might be a solid located on the edge of the slit. It might, therefore, be advisable to elongate the slit; for example, such an elongation could be as shown in Fig. 8, which is the same as shown in Fig. 7, except that the slit, instead of being two razor edges, consists of two blocks very close together, forming a very thin flat tube.

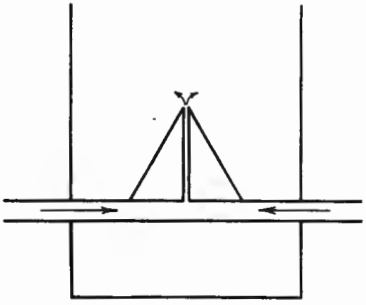

FIG. 8. ELONGATED STATIONARY SLIT

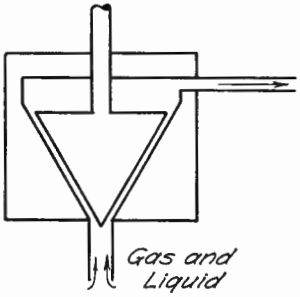

FIG. 9. STATIONARY CONE SLIT

This type of apparatus has one very distinct advantage, and that is that if the reaction takes place inside the elongated slit, the chances of removing the heat produced by a partial oxidation, for example, would be very good. It would be the same as having an extremely small catalytic tube except that the chance of plugging this tube is very slight because of its width and, therefore, its capacity can be made very great.

The elongated slit was changed to resemble a cone-shaped valve. A sketch of this apparatus is shown in Fig. 9. The gas and liquid enter at the bottom, the cone is adjustable at the sides, and the gas and liquid come out at the top. This is somewhat similar to certain types of homogenizers now on the market. This apparatus worked satisfactorily, but showed no particular advantage over the razor-edged slit.

V. ELONGATED SLITS WITH ONE SIDE IN MOTION

12. *Reasons for This Type.*—It was thought advisable, in order to eliminate any clogging, even in a very small machine, to have one side of the slit moving. This movement would have a tendency to produce even greater contact between the gas and the liquid. The sides of the slit are very close together, and any movement would have a tendency to break up bubbles of gas or globules of liquid.

13. *Rotating Disk Slit.*—The first machine developed of this type resembled somewhat a colloid mill. A sketch of this machine is given in Fig. 10. The bottom round plate (one inch in diameter) was stationary. It had an opening in the center which was connected with both the gas and liquid lines. The gas and liquid entered through a nozzle, which resembled a miniature injector, and were forced out

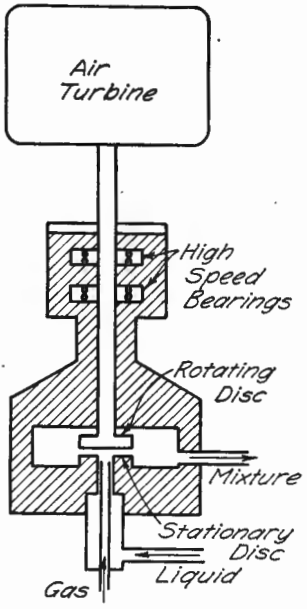

FIG. 10. ROTATING DISK SLIT

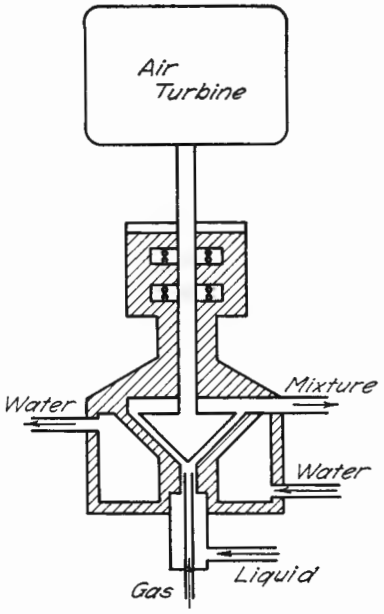

FIG. 11. ROTATING CONE SLIT

through the slit between the upper and lower disks. The upper disk was connected to a shaft which was operated by the air turbine previously mentioned, and rotated at a speed of ten to twenty thousand revolutions per minute. Special high-speed bearings were used to hold the shaft in place. The clearance between the lower and upper disks varied from one to three thousandths of an inch. This equipment was tested on the ethylene benzol reaction previously mentioned, and proved to be the most satisfactory machine for this particular gas reaction yet developed.

14. *Rotating Cone Slit.*—In order to take advantage of the elongated slit it was necessary to put in a cooling chamber against the permanent disk. It was thought advisable, however, to increase the surface of the sides of the slit in order to improve the heat transfer. A new design which proved very satisfactory is shown in Fig. 11. The revolving disk is changed into a revolving cone. This cone fits with a thousandth of an inch clearance into a cone-shaped cavity. The bottom of this cavity is the opening for the gas and liquid, with the same type of injector as shown in Fig. 10. Around the sides of the cone cavity is a cooling or heating chamber as the case may warrant. It should be

noted that the very rapid rotation of the cone tends to eliminate any stagnant liquid film on the surface of the metal cavity, thus preventing one of the chief reasons for the resistance to heat flow.

VI. Summary

15. *Summary.*—A review of the equipment now used for gas-liquid reactions has been given, together with a description of recent development work involving the use of stationary and revolving slits for the same purpose. This development is still in the laboratory stage. The commercial application is, however, a possibility.

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