Ammonia as a Source of Hydrogen for Hardening Oils

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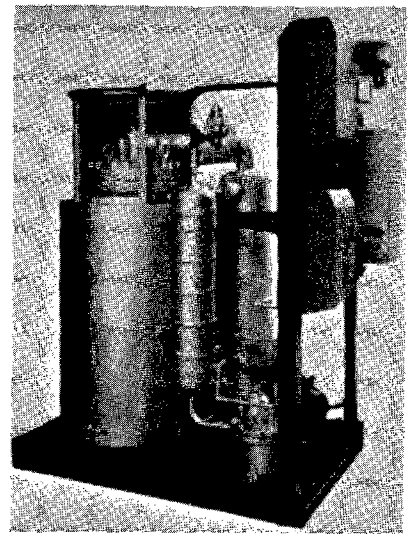

Experimental Ammonia Cracker. Designed to deliver 500 cu. ft. hydrogen per hour under pressure of 100-lb. gage.

Commercial liquid ammonia is made by catalytic high-pressure synthesis from the elements hydrogen and nitrogen, according to the reaction

$$3H_2 + N_2 = 2\,NH_3\ (\text{liquid}) + 42{,}000\ \text{cal.}$$

As is well known, this reaction is reversible. Conditions favoring reversion are high temperature and low pressure, especially in the presence of the same type of catalyst used for synthesis, that is, activated iron oxide. Upon this principle is based the ammonia dissociator or "cracker" developed by the du Pont Company.

The pressure range in which ammonia dissociation is practically complete is from sub-atmospheric up to about 15 atmospheres. For example, at atmospheric pressure and the normal cracking temperature of 600°C. the residual ammonia will be about 0.03 to 0.05% by volume, increasing to about 0.6% by volume at 15 atmospheres pressure. In any case, the ratio of hydrogen to nitrogen is exactly 3:1 or, stated in another way, the product is 75% hydrogen and 25% nitrogen by volume or 17.8% hydrogen and 82.2% nitrogen by weight, neglecting the residual ammonia content.

One pound of anhydrous ammonia upon cracking yields 45.4 cu. ft. of gas of which 75% or 34 cu. ft. is hydrogen, measured at one atmosphere and 21°C. or 70°F. Therefore 29.4 lb. of ammonia is required to produce 1,000 cu. ft. of hydrogen measured at these conditions. Allowing for residual ammonia from cracking, and for small losses in storage and handling, 30 lb. of ammonia per 1,000 cu. ft. of hydrogen is a very liberal allowance.

Present Applications

Heretofore, cracked ammonia has been used solely as a substitute for compressed cylinder hydrogen, or for other non-oxidizing gas mixtures. Since the large proportion of such hydrogen or gas mixtures is used at atmospheric pressure, the first cracker was designed to operate at this pressure. Nearly all of the crackers now in operation are used in the metallurgical industries for annealing and working metals, and for reducing metal oxides to pure metal. In these applications, residual ammonia in small proportion is not harmful, therefore the cracked gas is used direct.

Pressure Cracker Equipment

More recently, the du Pont Company has extended cracker development with the object of producing a gas under pressure, suitable for applications such as the hardening of oils. This scheme is attractive because the gas is available directly under pressure, without the use of compressor equipment. Furthermore, this result is accomplished without sensible decrease in cracking efficiency or increase in cost.

Although the pressure cracker equipment is not now being manufactured regularly, it is felt that sufficient development work has been done to demonstrate the technical feasibility and to warrant brief description of results thus far attained. The general features of design for the pressure cracker are the same as for the atmospheric cracker, except that the structure is pressure sustaining, and alloy metals are used for parts in contact with hot gas. The illustration is an unretouched photograph of a "homemade" cracker built in the du Pont shops. This cracker will deliver at 100 lb. gage pressure about 700 cu. ft. of gas per hour, equivalent to about 500 cu. ft. of hydrogen per hour or 12,000 cu. ft. of hydrogen per day of 24 hours. A cracker has been designed to deliver about 1,000 cu. ft. of hydrogen per hour or 24,000 cu. ft. per day, and to operate at any pressure up to 200 lb. gage. While still larger crackers doubtless could be built, it is probable that above units of 1,000 cu. ft. hydrogen per hour there would be no appreciable economies, either as regards first cost or operating cost. Therefore, when larger capacity is desired, a multiple-unit system is recommended.

Characteristics of Cracked Ammonia

Cracked ammonia produced at 100 lb. pressure will contain from 0.3 to 0.5% ammonia by volume, depending upon the manner in which the unit is operated, 0.3% being about the lower limit. Since this much residual ammonia is undesirable for oils hardening, a simple pressure water scrubber is provided, which reduces the residual ammonia practically to zero. The delivered gas contains only 0.2 to 0.3 lb. of water per 1,000 cu. ft., depending upon the water temperature. This proportion of water has been demonstrated not to be harmful in oils hardening. The quantity of water required for scrubbing is small, not more than 20 gal. per hour per 1,000 cu. ft. of hydrogen.

It should be stressed also that cracked ammonia made from technical-grade synthetic ammonia contains absolutely no catalyst poisons, such as carbon monoxide, or sulphur in any form.

Hardening of Oils

Sufficient experimental work has been done to indicate conclusively that cracked ammonia will harden oils satisfactorily. Oil has been hardened in batches of more than 1,000 lb., the product being normal in all specifications, including specifications for food use. All such experimental work has been carried out by companies in the oil industry in cooperation with the du Pont Company.

Because cracked ammonia contains only 75% hydrogen instead of nearly 100% hydrogen in gas from the steam-iron and electrolytic processes, several questions are pertinent, namely, what is the comparative rate of hardening, and what is the efficiency of hydrogen utilization? Disregarding the factors of temperature, catalyst activity, and ratio of catalyst to oil, it can be stated that the rate of hardening and efficiency of hydrogen utilization depend upon the pressure of hydrogen and upon the contact between gas and oil. The rate of hardening in a system which is properly designed to handle a large proportion of inert gas will be the same with cracked ammonia as with hydrogen from other sources, provided the hydrogen pressures are the same. For example, the rate of hardening with essentially pure hydrogen at 50 lb. absolute pressure (35 lb. gage) would be equaled with cracked ammonia (75% hydrogen by volume) at $4/3 \times 50 = 67$ lb. absolute pressure (52 lb. gage). As pointed out previously, an ammonia cracker has been designed to deliver gas at pressures up to 200 lb. gage.

As to efficiency of utilization, it has been found that 91% utilization of hydrogen in cracked ammonia can be secured. However, in order to realize satisfactory performance in large autoclave units, it is important that provision be made for adequate gas circulation, otherwise the desired hardening rate must be secured by excessive purging of gas. In a well-designed system, the inert nitrogen can be made to perform the useful function of agitation.

The extremely high purity of cracked ammonia with respect to catalyst poisons is a factor of importance. One user of steam-iron hydrogen estimates that freedom from catalyst poisons is equivalent to a credit of 20-30c per 1,000 cu. ft. of hydrogen. Obviously this is a factor which should be evaluated for each individual case.

Cost of Hydrogen from Cracked Ammonia

A distinct advantage of cracked am-

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monia is low capital cost. A cracker designed to deliver 1,000 cu. ft. hydrogen per hour at any pressure up to 200 lb. gage can be built for $2,500 complete with accessories and electrical equipment. This cost is assumed however for a unit to be part of regular production. Larger units doubtless could be built, although there would be little, if any, increased advantage, either in capital cost or in operating economy. In a multiple-unit system, economies can be affected in accessories and electrical control equipment, and such a system has a degree of flexibility that could not be attained in a larger unit of comparable capacity.

Storage facilities for liquid ammonia to handle one standard tank car (50,000 lb.) can be installed for about $6,000 including accessory piping and compressor. Therefore, the investment required to produce 1,000 cu. ft. of hydrogen per hour would be about $12,000 erected, including ammonia storage and spare cracker. Further, it has been estimated that the investment for a production of 5,000 cu. ft. of hydrogen per hour would be about $22,000 erected, including ammonia storage and 2 spare crackers.

The floor area required for cracked ammonia plant is relatively small, being only 20 $\times$ 20 ft. for a capacity of 5,000 cu. ft. per hour, but not including space for ammonia storage. Headroom of 6 ft. is sufficient.

As regards operating cost, by far the largest item is for ammonia. The present price of technical grade anhydrous ammonia in tanks of 50,000 lb. is 4½c per lb. at works, which means in most territories not more than 5c delivered. Therefore, the ammonia cost will not usually exceed $1.50 per 1,000 cu. ft. of hydrogen. Power required for cracking is approximately 17 kw. hr. per 1,000 cu. ft. of hydrogen. Catalyst cost is practically negligible, as with ordinary care a charge should last one year or longer. Operation of the cracker is practically automatic and very little labor is required for operation or repairs, as has been demonstrated with existing units. An allowance of 30c per 1,000 cu. ft. of hydrogen is considered ample to cover the cost of power, repairs, and labor, therefore the cost of hydrogen exclusive of fixed charges is approximately $1.80 per 1,000 cu. ft. Depreciation at 10% and taxes and insurance at 2% per year are equivalent to 20c per 1,000 cu. ft. for an output of 1,000 cu. ft. per hr. and 7c per 1,000 cu. ft. for an output of 5,000 cu. ft. per hr.

Costs for outputs less than 1,000 cu. ft. per hour would not increase appreciably, a point to be considered by those who have small outputs of hardened oil, or who desire to decentralize their operations and thus reduce freight expense on incoming oil and outgoing product.

In comparing the cost of hydrogen from various processes, some credit must be given hydrogen from cracked ammonia because of freedom from catalyst poisons, and because it is delivered under pressure. Obviously, it is difficult, if not impossible to generalize in the matter of cost comparisons, and yet cover all cases adequately and fairly. For that reason, it is recommended that detailed comparisons be prepared only for specific cases based on the particular local conditions.

Summary and Conclusions

Equipment for dissociating or "cracking" ammonia has been developed to deliver catalytically pure hydrogen under pressure. The cracker is practically automatic in operation, occupies but small space, and can be built to meet a wide range of capacity operating at high economy. While it is not claimed that cracked ammonia is the preferred source of hydrogen for large outputs, it should be considered for any requirement of less than 1,000 cu. ft. per hour, and in some cases for requirements of 1,000 cu. ft. and more. Cracked ammonia has been demonstrated to be suitable for hardening oils, and affords a source of cheap hydrogen with a minimum investment for those who desire to operate on small scale or who desire to decentralize large operations.