Use of Dissociated Ammonia for Hydrogenation*

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THE idea of producing hydrogen gas from dissociated ammonia and using the hydrogen for hydrogenation purposes is not new. However, if published data may be taken as criteria, little experimental work has been done in the past. Possibly this has been due to the economic features involved. The current price of ammonia, plus the price and efficiency of dissociation equipment, indicates that it is possible to produce hydrogen for hydrogenation economically by this method.

Preliminary Considerations

In considering this method for producing hydrogen and subsequent use of the hydrogen for hydrogenation, two unknown factors require consideration:

1. Is the use of dissociated ammonia economically attractive? This feature is also composed of two factors:
    - a) Efficiency of hydrogenation from hydrogen so produced.
    - b) Cost of producing hydrogen from ammonia.
2. Activity of hydrogen:
    - a) Effect of nitrogen as a hydrogen diluent.
    - b) Efficient hydrogenation with mixed hydrogen and nitrogen.
    - c) Effect of nitrogen on the catalyst activity.
    - d) Removal of residual ammonia from the mixed gases.

We will first discuss Item 1 on the economics of using dissociated ammonia for hydrogenation. Calculations in 1946 revealed that a small hydrogen plant of the propane type would necessitate an investment of about $100,000. The capacity of this plant would be 2,000 cu. ft./hour. On this basis (operating 300 days/year), the cost of producing hydrogen would be $2.04 per 1,000 cu. ft.

On the same basis an ammonia dissociating plant producing 1875 cu. ft./hour (2,500 cu. ft./hr. mixed gases) would entail an investment of $17,000 and would produce hydrogen at a cost of $1.97 per 1,000 cu. ft. The cost of housing the equipment is not included, and calculations are based on a cost of ammonia of $0.0365/lb. in tank cars. Ammonia unloading facilities also have not been included. The use of cylinder ammonia at about 15 cents per pound is of course uneconomical.

It should be borne in mind that, due to the initial cost of the propane plant, the cost of hydrogen increases rapidly with a smaller demand while the ammonia dissociation process becomes economically more attractive. It is also obvious that the ammonia dissociation process would have greater flexibility in the event larger hydrogen requirements than anticipated were needed.

As the use of dissociated ammonia for hydrogenation was found to be economically attractive, we proceeded with the technical aspects of the process.

Equipment

The ammonia dissociator used was built by the Drever Company of Philadelphia. Its capacity was 100 cu. ft. per hour. This unit was equipped with absorption towers containing aluminum oxide. Cylinder ammonia was used for this unit and the vapor pressure in the cylinders was sufficient to maintain a flow of 100 cu. ft. per hour successfully.

A Wayne air compressor with a horizontal 60-gallon tank was installed to collect the mixed gases. A surge tank was connected between the dissociator and the compressor. The volume of the high pressure storage tank at standard conditions was 8.05 cu. ft. of gas.

The hydrogenators used were of the autoclave type of 20-gallon and 2-gallon capacity.

Necessary gauges, thermometers, check valves, etc., were installed for control. A rotometer was used to measure the flow of mixed gases.

Measurement of Gas Consumed

A method was developed for the estimation of the hydrogen gas consumption. The exact volume of the high pressure storage tank was determined from its water displacement. A dead weight tested pressure gauge and a Fahrenheit thermometer were installed on this tank. By knowing the volume of the tank, the pressure drop, and the temperature change, utilization of the simple Gas Law gave us a means of estimating gas consumption.

The derivation is as follows:

a) $PV = \frac{n}{359} RT$

where

P = Pressure in lb./sq. inches absolute
V = Volume in cu. ft. = 8.05
$\frac{n}{359}$ = Moles of gas (n in cu. ft.)
R = Proportionality constant = 10.71
T = Absolute temperature (R° = °F. + 460)

b) Derived formula

$$\text{Cu. ft. of gas at S.T.P.} = \frac{(P_1T_2 - P_2T_1)}{T_1T_2} 270$$

The method chosen for expressing hydrogen consumption was cu. ft./iodine value/ton and the following formulae were derived and used:

a) Pure hydrogen

$$\text{Cu. ft. hydrogen/IV/ton} = \frac{\text{cu. ft. gas used} \times 2{,}000 \text{ lbs.}}{\triangle \text{ I. V.} \times \text{oil wt. used}}$$

b) Dissociated ammonia

$$\text{Cu. ft. hydrogen/IV/ton} = \frac{\text{cu. ft. gas used} \times 2{,}000 \text{ lbs.} \times .75}{\triangle \text{ I. V.} \times \text{oil wt. used}}$$

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Δ I. V. represents the change in iodine value during the specific conditions of any of the experiments. Inasmuch as dissociated ammonia consists of 3 volumes of hydrogen to 1 of nitrogen, a factor of 0.75 was indicated. In order to compare the experimental hydrogen consumption figures with the theoretical amount required, it was necessary to calculate the theoretical value. As one pound of iodine reacts with 100 pounds of oil (definition of iodine number), 20 lbs. of iodine reacts with 1 ton of oil.

$$\frac{20}{253.86} \text{ (moles of iodine)} \times 359 \text{ (cu. ft. in a mole of gas)} = 28.3$$

The theoretical consumption is 28.3 cu. ft. H_2 per I. V. drop per ton of oil.

Development of a Hydrogenation Method for Triglycerides

As is well known, the customary batch hydrogenation method, using commercially pure hydrogen, is accomplished in a closed reaction vessel connected to a hydrogen source. Although small amounts of inert gases are present in these hydrogens, their concentrations never reach a value which seriously affects the rate of hydrogenation. However, inasmuch as dissociated ammonia contains 25% nitrogen, it becomes a serious hindrance to hydrogenation.

With the gas measurement technique developed we proceeded to investigate a practical method of hydrogenation. The two methods investigated were:

1) An adaptation of the Conventional Batch Method.
2) Continuous Vent-constant Pressure Method.

Method No. 1 was first investigated. At that time the ammonia dissociator had not been installed and a mixture of cylinder nitrogen and cylinder hydrogen was used. The mixtures of gases, comparable to dissociated ammonia, was introduced into an evacuated 20-gallon saturator containing 100 lbs. of refined and bleached soya bean oil and commercial nickel catalyst. When the increased nitrogen concentration became apparent through the decrease in reaction rate, no more gas was introduced. The decreased rate was apparent through the attainment of a pressure equilibrium when the hydrogenation was isolated in this manner.

At this point the hydrogenation was allowed to proceed 12 minutes longer. It was hoped that maximum utilization of the hydrogen would be realized. Table I lists the results of this work.

TABLE I

Run No.	Type of Gas	Temp. Range (°F.)	C.F.H./ I.V./Ton	ΔI.V./ Min.
1....................	Cylinder hydrogen	260-325	30.5	0.83
2....................	Cylinder hydrogen	260-325	28.5	1.20
3....................	75% hydrogen 25% nitrogen	260-325	47.5	0.07
4....................	75% hydrogen 25% nitrogen	260-325	33.5	0.07
5....................	75% hydrogen 25% nitrogen	260-325	39.4	0.06

From this data it is obvious that:

1) In the case of runs 3, 4, and 5 the hydrogen consumption per unit iodine value drop was excessive.
2) The time of hydrogenation per unit iodine value drop was excessive.

These two factors ruled this method impracticable.

Continuous Vent-constant Pressure Method

The second method investigated was based on the assumption that the hydrogenator could be used as a fractionator of the mixed gases. Ideally the gaseous mixture would enter the bottom of the hydrogenator and, on travelling up through the oil, the hydrogen would react with the oil and be absorbed and pure nitrogen would fill the head space of the reaction vessel. By venting the nitrogen at a rate equivalent to its influent rate, equilibrium would be established and hydrogenation would proceed, affected solely by the partial pressure of the hydrogen.

Table II shows the results of preliminary runs, using a vented converter and mixed gases.

TABLE II

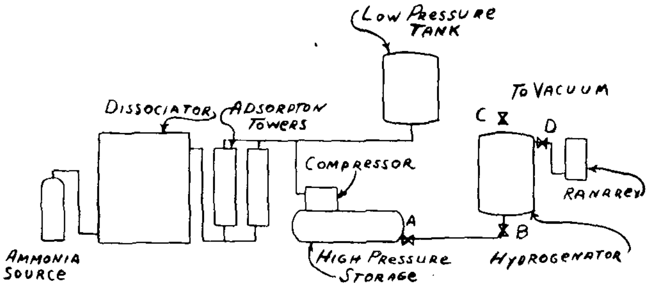
Run No.	Type of Gas Used	Temp. Range (°F.)	C.F.H./ I.V./Ton	ΔI.V./ Min.	Remarks
2..............	Cylinder hydrogen	260-325	28.5	1.20	No vent
6..............	75% hydrogen 25% nitrogen	260-325	28.6	0.22	Continuous purge
8..............	75% hydrogen 25% nitrogen	260-300	40.9	0.26	Increased cont. purge

These results were very encouraging and a more comprehensive investigation was undertaken. A description of equipment and method follows:

Equipment and Method Used

As indicated in the diagram the equipment consisted of the dissociator, aluminum oxide towers, a low pressure holding tank, compressor, high pressure storage tank, a hydrogenator, and a gas density meter of the Ranarex type.

DIAGRAM



The continuous vent-constant pressure method was accomplished in this equipment as follows:

1. A weighed amount of oil or fat (about 100 lb.) and catalyst was drawn into the hydrogenator and heated to 250°F. under vacuum and mechanical agitation (valves B and D closed, valve C open).

2. Dissociated ammonia or steam-iron hydrogen was compressed into the high pressure storage tank to about 190 lbs./sq. inch absolute.

3. The high pressure storage tank and the hydrogenator were isolated from the rest of the system. (Valves A, B, C, and D closed.)

4. Valve B was opened wide and valve A was opened slowly. The gases flowing through A entered

the hydrogenator in which the pressure began to rise. When a gauge pressure of 50 lbs./sq. inch was attained on steam-iron gas and 72 lbs./sq. inch in the case of dissociated ammonia, valve A was closed. Then initial readings of pressure and temperature in the high pressure storage tank were recorded.

5. Again agitation was applied to the material in the hydrogenator, and hydrogenation was begun. The pressure was controlled in the hydrogenator at 50 or 72 lbs. gauge by throttling valve B and opening wide valve A.

6. When the pressure in the high pressure storage tank reached about 80 lbs. gauge, valve A was closed and the final pressure and temperature readings were recorded. Hydrogenation was continued until the gauge pressure in the hydrogenator reached 50 lbs./sq. inch in the case of the steam-iron gas and 72 lbs./sq. inch in the case of the dissociated ammonia. Thus, initial and final conditions were the same, and the accuracy of gas consumption figures was within the limits of experimental error in the method.

When the hydrogenation was completed, a sample was drawn for an iodine value determination. Knowing the weight of oil used, the change in iodine value (Δ I.V.), the volume of the storage tank and the pressure and temperature changes of the gases in the storage tank, it was a simple matter to calculate the hydrogen consumption using the equations developed.

TABLE III

Run No.	Time, Minutes	Temp. Range (°F.)	ΔI.V.	I.V. Drop, Minutes	C.F.H$_2$/ I.V./ Ton	Vent (Roto-meter	Final I.V.
1	18	288-366	33.4	1.857	30.1	None	78.2
2	15	273-314	12.3	0.811	30.9	None	98.7
3-a	10	267-323	16.8	1.680	32.5	None	94.2
3-b	5	322-343	15.1	3.020	31.0	None	79.1
Control Avg.	12	288-336	19.4	1.84	31.1	91% Hydrogen Use Efficiency	

The difference in gauge pressure between steam-iron hydrogen and dissociated ammonia is due to the partial pressure in steam-iron hydrogen being approximately equal to the total pressure while dissociated ammonia contains only 75% hydrogen and the partial pressure equals only three-fourths of the total pressure. A gauge pressure of 72 lbs./sq. inch in the case of dissociated ammonia is equivalent to a hydrogen partial pressure of 50 lbs.

It was necessary to have the initial and final pressure in the hydrogenator equal because the pressure drop in the high pressure storage tank was used to calculate the amount of gas consumed. If the initial and final pressure in the hydrogenator were equivalent, then the hydrogen measured would equal the hydrogen absorbed.

At the beginning of our work a rotometer was used to control the composition of the vent gas. This was found a poor control as the specific gravity of the gas varied with its composition. Later an accurate vent rate control was accomplished by means of a Ranarex gas density meter. In using the Ranarex instrument a specific gravity value was used which indicated a gas vent effluent of 20% hydrogen and 80% nitrogen.

In Table III we list control hydrogenations, using purified steam-iron hydrogen and cottonseed oil.

The average values of the control runs shown at the bottom of the table are representative of the efficiency of purified steam-iron hydrogen in the equipment used.

TABLE IV

Run No.	Time, Minutes	Temp. Range (°F.)	ΔI.V.	I.V. Drop, Minutes	C.F.H$_2$/ I.V./ Ton	Vent (Roto-meter)	Final I.V.
1-a	43	248-267	19.1	0.444	32.6	25	92.5
1-b	37	276-330	21.9	0.592	29.2	25	70.6
2-a	54	242-258	14.4	0.266	34.4	25	97.2
2-b	32	260-372	18.1	0.565	36.3	25	79.1
3-a	32	248-364	19.9	0.622	32.6	25	91.7
3-b	32	353-370	19.8	0.620	31.6	25	71.9
4-a	36	256-290	18.3	0.590	34.9	25	93.3
4-b	19	282-328	21.4	1.127	29.2	....	71.9
5-a	43	240-262	16.4	0.381	38.0	25	95.2
5-b	34	256-289	21.4	0.269	30.4	25	73.8
6-a	36	254-303	20.5	0.570	31.0	25	91.1
6-b	32	296-314	18.6	0.581	33.2	25	72.5
7-a	35	255-352	20.1	0.574	31.0	25	91.5
7-b	40	352-375	22.8	0.570	28.7	25	68.7
Avg. a's	40	251-303	18.4	0.492	33.5	84.5% Hydrogen Use Efficiency	
Avg. b's	32	299-340	20.7	0.618	31.2	91.1% Hydrogen Use Efficiency	

In Table IV we list 14 individual hydrogenations on which the gas used was dissociated ammonia.

In comparing the average values from Tables III and IV, it is evident that the only marked difference occurs in the rate of hydrogenation. Too much weight was not placed on that factor at that time because it was believed firmly that improved experience and controls on the hydrogenation technique, using dissociated ammonia, would overcome this apparent handicap.

Hydrogenation of Lard to Flakes

Control Hydrogenations-Lard

The lard used in this series of runs was a refined prime steam lard. Table V lists the control data acquired using purified steam-iron hydrogen gas.

TABLE V

Run No.	Time in Minutes	Temp. Range (°F.)	ΔI.V.	I.V. Drop Minutes	C.F.H$_2$/ I.V./ Ton	Vent (Roto-meter)	Final I.V.
1	191	250-355	35.0	0.183	33.0	None	35.0
2	100	251-374	31.4	0.344	30.4	None	38.6
3	201	250-371	58.2	0.291	29.8	None	11.8

Average C.F. Hydrogen/I.V./Ton = 31.1
Average I.V. Drop/Min. = 0.273
Average Hydrogen Use Efficiency = 91%

The average figures from Table V compare favorably with respect to use efficiency with the results obtained in hydrogenating cottonseed oil. The slower hydrogenation rate of lard is generally noticeable.

Dissociated Ammonia Hydrogenations-Lard

Again in these hydrogenations the lard used was a refined prime steam lard. Table VI is a compilation of the data produced by these hydrogenations.

Gas was vented at a rate such that the specific gravity of the purge gas was 0.79 to 0.80.

As the hydrogenation progressed and the rate of hydrogen absorption decreased, the vent gas, for a constant vent valve setting, began to increase in the concentration of hydrogen. This change was detected by the Ranarex instrument and was corrected by throttling the vent valve until the specific gravity returned to the chosen value of 0.80.

It was apparent from these hydrogenations that:

1. Nitrogen had no apparent poisoning effect on nickel catalyst.

2. An efficient batch hydrogenation method had been developed, using dissociated ammonia.

3. The residual ammonia could be removed from the cracked gas.

TABLE VI

Run No.	Time in Minutes	Temp. Range (°F.)	ΔI.V.	I.V. Drop, Minutes	C.F.H_2/ I.V./ Ton	Vent (Rotometer)	Final I.V.
2-a	76	255-365	22.6	0.297	29.4	25	47.4
2-b	75	362-368	20.6	0.275	30.8	25	26.8
2-c	79	358-366	18.2	0.231	36.0	25	8.6
2-d	180	344-366	7.3	0.040	92.2	25	1.3
3-a	64	262-362	21.8	0.341	32.3	25	48.2
3-b	81	330-362	19.8	0.244	34.7	25	28.4
3-c	87	292-362	16.2	0.186	38.3	25	12.2
4-a	30	358-366	23.0	0.767	30.8	25	47.0
4-b	65	361-366	20.9	0.322	31.2	25	26.1
4-c	131	363-366	15.2	0.116	42.4	25	10.9
5-a	30	266-302	22.9	0.764	31.2	Ranarex Used[1]	47.1
5-b	20	302-370	25.3	1.265	26.8	Ranarex Used[1]	21.8
5-c	115	362-370	21.0	0.183	29.2	Ranarex Used[1]	0.8
6-a	51	254-365	26.2	0.514	29.5	Ranarex Used[1]	43.8
6-b	70	345-368	23.2	0.332	28.3	Ranarex Used[1]	20.6
6-c	134	361-365	17.8	0.133	35.9	Ranarex Used[1]	2.8
6-d	246	354-358	2.3	....	183	....	0.5
7-a	53	288-363	21.3	0.402	31	Ranarex Used[1]	48.7
7-b	50	279-362	21.0	0.420	32.5	Ranarex Used[1]	27.7
7-c	167	358-366	16.9	0.101	37.2	Ranarex Used[1]	10.8

[1] Setting at 0.80 specific gravity (80% N_2+20% H_2).

4. The hydrogen consumption efficiency was equal to or better than that obtained by using purified steam-iron gas.

We would like to present further data on the use of this method for the conversion of nitriles to primary amines, and also the hydrogenation of unsaturated fatty acids.

The equation expressing the conversion of nitriles to primary amines may be written as follows:

$$RC - N + 2\,H_2 \rightarrow RC\,H_2\,NH_2$$

The desired end product in the hydrogenation of nitriles is one containing as high a concentration of primary amine as possible, and this concentration is determined by titration of the amine sample using a standardized acid solution.

Qualitative hydrogenations were accomplished using 10-pound samples of nitriles. Table VII lists the pertinent data, using both purified steam-iron hydrogen and dissociated ammonia as hydrogenation gases.

TABLE VII

Hydrogenations

Run No.	Gas Used	Primary Amine Yield
1	Purified steam-iron hydrogen	92.1
2		92.4
3		90.3
1	Dissociated ammonia	88.5
2		88.7
3		88.7
4		89.0
5		94.3

It was apparent from the data listed in Table VII that nitriles were hydrogenated to primary amines in satisfactory yields using cracked ammonia.

The fatty acid hydrogenations also were accomplished in the one-gallon sized hydrogenator. Five-pound quantities of fatty acids were hydrogenated using dissociated ammonia. No purified steam-iron hydrogen controls were required and no attempt was made to determine the hydrogen consumption figures. All data is given in Table VIII.

TABLE VIII

Fatty Acid Hydrogenations

Run No.	Time, Minutes	Temp. Range, °C.	Final Iodine Value
1	90	115-235	4.4
2	60	166-263	6.6
3	30	182-232	5.7
4	40	155-180	7.1
5	70	115-236	6.6
6	95	115-240	4.8

The hydrogenation of fatty acids to sufficiently low iodine values was accomplished through the use of dissociated ammonia. This is apparent in the data of Table VIII.

General Conclusions and Remarks

On the basis of the experimental data assembled, the following conclusions may be stated regarding the use of dissociated ammonia gas:

1. Edible and inedible fat and oil can be hydrogenated successfully using dissociated ammonia.
2. Lard was hydrogenated to iodine values below 5.
3. Nitriles were hydrogenated to primary amines in satisfactory yields.
4. Fatty acids were hydrogenated to iodine values below 5.
5. Dissociated ammonia can be used successfully in any hydrogenation to which the "continuous vent-constant pressure" method can be adapted.
6. Hydrogen gas consumption was comparable to results obtained using hydrogen gas from other sources.
7. The ammonia dissociator, as a hydrogen production unit, can compete favorably with other hydrogen producing units, depending upon the capacity requirements.
8. As an added feature, the operation of an ammonia dissociator is exceedingly simple and lends itself readily to automatic control. It may be operated efficiently at any through-put rate up to its rated capacity, and in many instances this flexibility would prove to be valuable. Also, the gas contains no impurities harmful to hydrogenation catalysts and thus eliminates the necessity for complex purification processes.