

Hydrogen Supply Options and Issues

Kathleen A. Kuberka*, Mark K. Weise and Celeste A. Messina

Linde Division, Union Carbide Corporation, Tarrytown Tech. Center, Old Saw Mill River Road, Tarrytown, NY 10591

Methods of hydrogen gas production for hydrogenation are discussed: steam reforming of natural gas, electrolysis, by-product clean-up by PSA (pressure swing absorption) or scrubbing, and others. Hydrogen can be obtained from a customer-owned hydrogen plant or as a merchant product supplied by an industrial gas supplier. The merchant product can be delivered in trailers as gas, liquid-high (up to 2,200 psig), low pressure (up to 130 psig), or supplied over the fence from a pipeline or hydrogen generating plant. Several factors must be considered in selecting an optimum supply, including availability and cost of capital and of operating labor, use patterns, average demand, instantaneous demand, use pressure, growth projections, and purity requirements. Recent field test data have shown that increased hydrogen purity can improve the hydrogenation processes.

Hydrogenation is an extremely important process in fats and oils processing technology. Used with a catalyst, hydrogen converts the double bonds in unsaturated oils to single bonds creating stable saturated fats. It also changes liquid oils to semi-solid, hard, or plastic fats, soft fats to firmer products, and oils to value-added oleochemicals.

Typical methods of hydrogen gas production for hydrogenation include: steam reforming, electrolysis, ammonia dissociation, and merchant supply.

The decision for the optimum supply method of the hydrogen involves many considerations including average flowrate, instantaneous flowrate, use pattern, use pressure, availability and cost of capital, operating costs, and the impact on hydrogenation processing costs.

Because of flowrate requirements and desire for low hydrogen production costs, most fats and oils processors choose the steam reformer with a monoethanolamine (MEA) purification system as the method of supply. However, the impact of purity on hydrogenation processing costs and product quality has become an important issue.

Recent field test data has shown that increased hydrogen purity can improve hydrogenation processes by decreasing batch times, decreasing hydrogen use, and improving batch consistency. The benefits obtained with high purity hydrogen could offer substantial economic advantages to hydrogenation processors.

High purity hydrogen sources—such as Steam Reformers with PSA Purification Systems or Merchant Hydrogen Supply Systems—should be strongly considered and evaluated as the preferred supply method.

PROCESSES DESCRIPTION

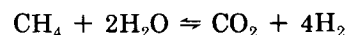
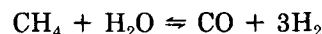
Steam reforming. Hydrogen is produced by catalytically

reforming natural gas (or other hydrocarbon fuels) with superheated steam at elevated temperatures in a vertical reformer furnace.

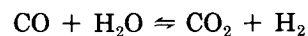
The basic steps for the steam-hydrocarbon reforming process (Fig. 1) are desulfurization, reforming, CO conversion, and purification. The desulfurization of the hydrocarbon feed is necessary in order to prevent catalyst deactivation or poisoning. Depending on the type of feedstock and the nature of the sulfur contaminants, desulfurization methods can vary from ambient temperature adsorption on activated carbon to a high temperature reaction with zinc oxide.

A typical reformer is an up-flow, bottom fired furnace operating up to 1700°F. The desulfurized hydrocarbon fuel and steam are fed to a vertical bank of reactor tubes suspended inside the furnace. These tubes are filled with a nickel based reformer catalyst. The hydrocarbon fuel provides both the process feedstock for the reaction and a portion of the heat necessary to sustain it.

Radiant and convective heat generated inside the furnace is conducted through the tubes to the reacting gases. The formation of hydrogen inside the catalyst packed tubes occurs based on the following equations using natural gas:



The reformed gas contains hydrogen, carbon monoxide, carbon dioxide, unreacted hydrocarbon, and excess steam. The gas is cooled and passed through a shift converter where the carbon monoxide is reacted with steam to produce additional hydrogen by the following reaction:



The two most common methods of purification to remove or reduce the impurities of carbon monoxide, carbon dioxide, and hydrocarbon fuel from the crude hydrogen stream are shown in Figure 2.

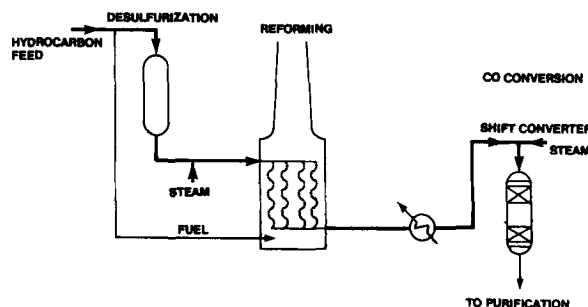


FIG. 1. Steam reformer.

*To whom correspondence should be addressed.

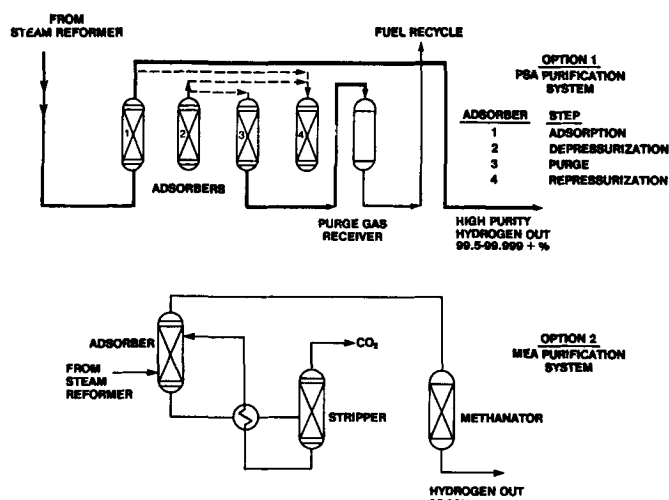


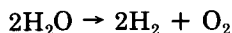
FIG. 2. Steam reformer purification systems.

For a high purity hydrogen product (99.5–99.999+%) a Pressure Swing Adsorption (PSA) unit is utilized. The PSA system uses four vessels, each having a bed of activated alumina, carbon, and molecular sieves. The adsorption system operates on a repeated cycle with two basic steps, adsorption and regeneration. Approximately 75–80% of the hydrogen in the PSA feed is recovered. The unrecovered hydrogen and impurities are separated from the feed gas and returned to the reformer burners as fuel. This gas provides 75–85% of the furnace heat requirements. The balance is provided by burning natural gas.

Another purification method produces hydrogen of purities 95–98% and is less capital intensive than the PSA approach.

The raw hydrogen stream is cooled and scrubbed using a monoethanolamine (MEA) solution to remove most of the carbon dioxide. The remaining carbon dioxide and carbon monoxide impurities are removed by heating the gas and passing it through a nickel based methanation catalyst where the carbon oxides are reacted with the hydrogen to form methane.

Electrolysis. Hydrogen is produced by the electrolytic decomposition of alkalized water into its basic elements according to:



A typical system consists of cell banks made-up of individual cell compartments having an iron cathode and a nickel-plated iron anode separated by a laminated asbestos diaphragm. The alkaline electrolyte solution enters the cell on the cathode side and then flows to the anode. The system is shown in Figure 3.

The generated hydrogen/catholyte mixture from the cathode side is sent to a separator. The separator is cooled by a tempered water system to remove heat generated by the electrolyzer. The hydrogen is then water cooled and passed through a knock-out pot for final water removal. Hydrogen gas purity is typically 99.7%. The product hydrogen is often further dried and passed through a deoxo unit to remove trace oxygen, which increases the purity to 99.9%.

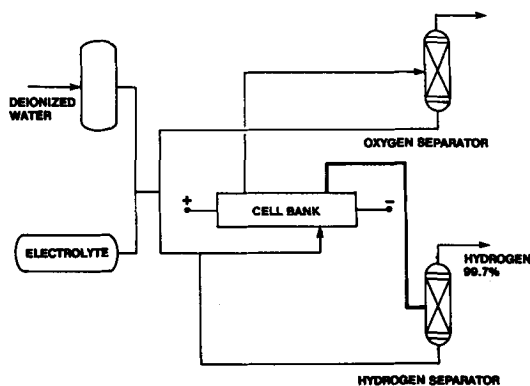


FIG. 3. Water electrolysis.

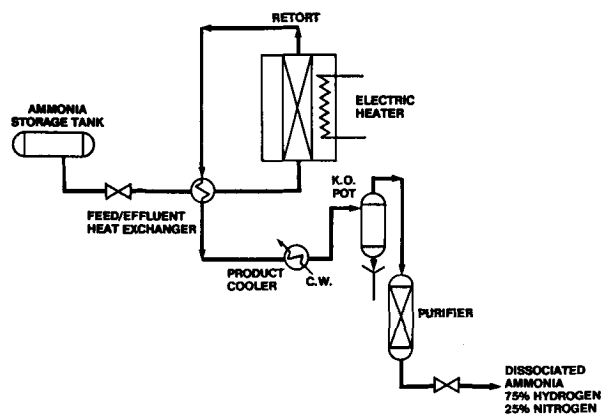
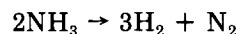


FIG. 4. Ammonia dissociation.

Ammonia dissociation. Hydrogen is produced by the cracking of gaseous ammonia into its components as follows:



The process consists of vaporizing liquefied anhydrous ammonia and passing it through a heated retort chamber which contains an active nickel catalyst. The cracked ammonia is then cooled and purified over activated carbon to remove any residual water or ammonia (Fig. 4).

Hydrogen gas purity is 75% with the balance nitrogen.

Merchant supply. Merchant hydrogen is hydrogen offered for sale by an industrial gas supplier. The hydrogen can be produced by steam reforming of natural gas, by-product recovery using pressure swing adsorption (PSA) purification technology, or cryogenic separation.

Hydrogen is delivered in either gaseous or liquid form to be stored and utilized as required. Typical hydrogen purity is 99.999%.

Transported gaseous hydrogen is delivered in tube trailers and is stored in high pressure (2400 psig) gaseous storage receivers. Hydrogen gas is supplied upon demand through a pressure regulator station.

Liquid hydrogen is transported in cryogenic trailers and is stored in double-shell, vacuum-insulated cryogenic tanks at pressures up to 150 psig. It is then vaporized for process use with atmospheric, steam, or electric

HYDROGEN SUPPLY OPTIONS AND ISSUES

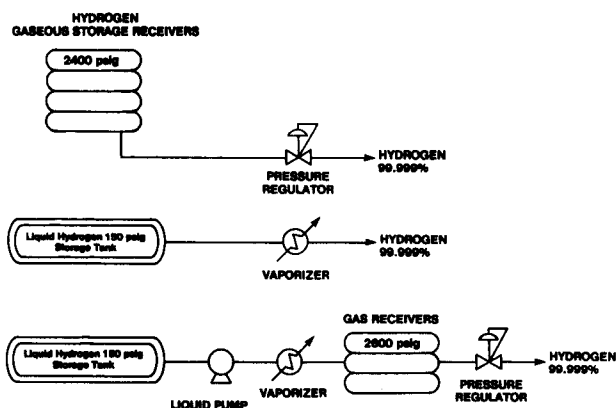


FIG. 5. Merchant supply options.

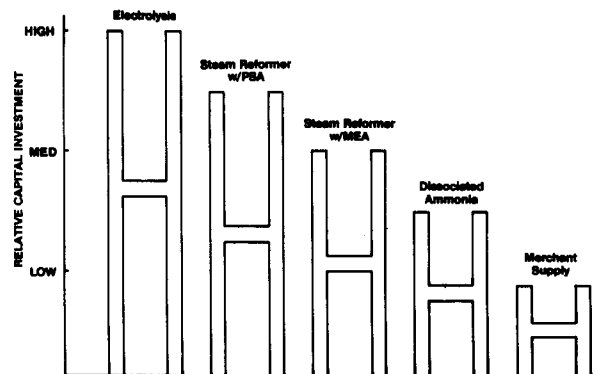


FIG. 7. Capital investment.

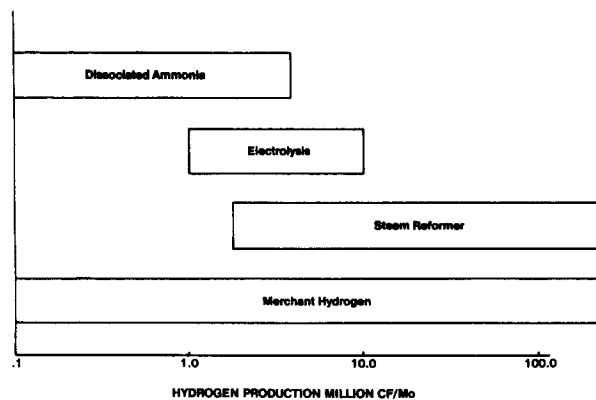


FIG. 6. Hydrogen system size ranges.

vaporizers. Higher pressures (up to 2600 psig) are provided by installing a cryogenic liquid pump. Some merchant systems are shown in Figure 5.

Other merchant gaseous hydrogen supply options include pipeline supply and dedicated over-the-fence supply via steam reformer operation or hydrogen by-product recovery which uses PSA technology.

COMPARATIVE STUDY

When a new hydrogen supply system is evaluated parameters that are usually investigated are hydrogen flow rate, capital investment, and operating costs. For existing systems, operating costs and the impact on hydrogenation processing costs are on-going concerns.

The hydrogen flow rate requirement will direct the initial choice of the supply system. The use pattern of the hydrogen must be carefully investigated so that a proper design flow rate can be chosen. Instantaneous peak demands, as well as the base load, must be considered. Hydrogen system size ranges are shown in Figure 6. Merchant hydrogen offers the greatest flexibility in terms of flow rate range and meeting peak demands. Steam reformers are applicable for high hydrogen flow rates (2 MMCF/month and up), whereas electrolysis and dissociated ammonia are applicable for the lower hydrogen flows (less than 10 MMCF/month).

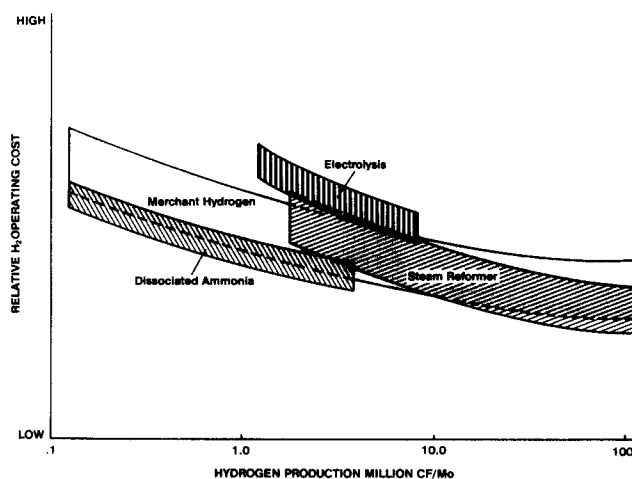


FIG. 8. Hydrogen operating cost.

With nonmerchant supply modes, thought must be given to an appropriate peak handling system. On-site gas storage tanks are often installed or merchant hydrogen is used to meet the peak demands.

Capital investment for new equipment must take into account the availability and cost of capital. Figure 1 shows the relative capital investments for installed hydrogen supply options. In general, electrolysis equipment and steam reformers with PSA clean-up systems will be at the high cost end while merchant supplied systems will be at the low cost end of the scale. Assuming the capital is available to buy the equipment, the money is included into the operating costs of the system in terms of depreciation and return on investment.

Operating costs of the system include raw materials, utilities, labor and maintenance. Fixed costs include taxes, insurance, and administration expense. Depending on the utilization of the system, the unit cost of the product can have a wide variance. In Figure 8, relative operating cost positions for the four supply modes are shown. It can be seen that a large amount of overlap occurs between the supply systems.

Increasingly, differentiation between methods of supply will include the effects on processing where hydrogen purity can play a major role. The contained impurities of the different supply modes are shown in Figure 9. To quantify some of the effects of purity on hydrogenation

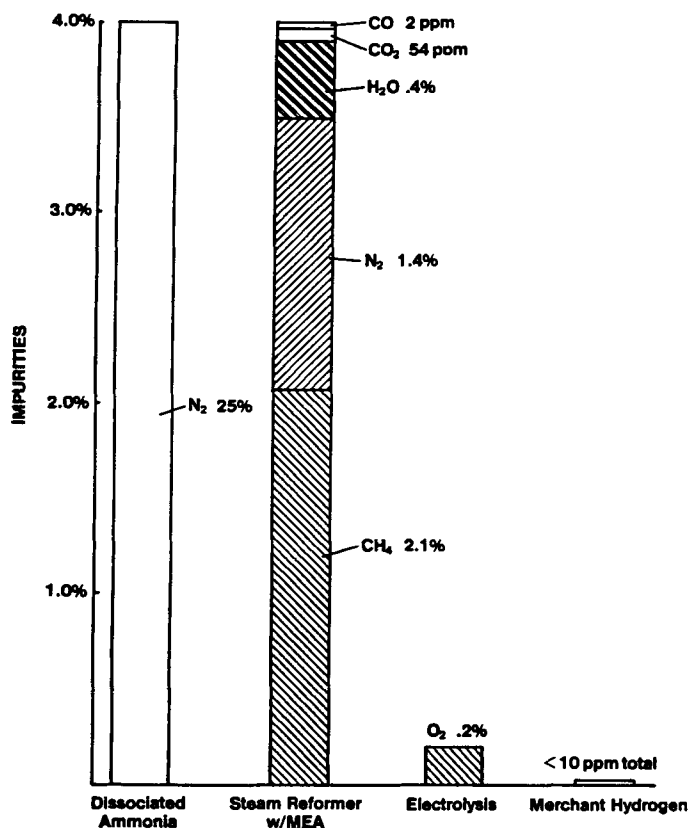


FIG. 9. Contained impurities.

processing, a field test was run in order to evaluate the effect of utilizing high purity merchant hydrogen versus steam reformer (MEA purification) generated hydrogen for the hydrogenation of soybean oil. The test and results are discussed below.

HYDROGEN PURITY TEST PROGRAM

The test program was performed at a commercial fats and oils manufacturing facility producing vegetable oil.

Test program objectives. To characterize the current hydrogen gas generated by an on-site steam reformer with MEA purification system. To evaluate the effect of utilizing high purity hydrogen (merchant supplied) versus steam reformer (with MEA purification) generated hydrogen for the hydrogenation of soybean oil.

Test program. The high purity hydrogen source was liquid hydrogen using a portable supply system.

The hydrogen purity test program involved two stages. First, the feed and headspace gases of hydrogenators were monitored to establish typical or "base case" operation. Secondly, the steam reformer was shut down and the supply switched over to merchant supplied liquid hydrogen. A scheme of the analysis system is shown in Figure 10. Sample lines were run from the hydrogen feed line and vent line for each reactor. Gas analysis data was recorded for both the feed and vent lines over the course of the hydrogenation cycle. Batch time data and product specifications were taken from the data base maintained by the clinet. A list of test parameters is shown in Table 1.

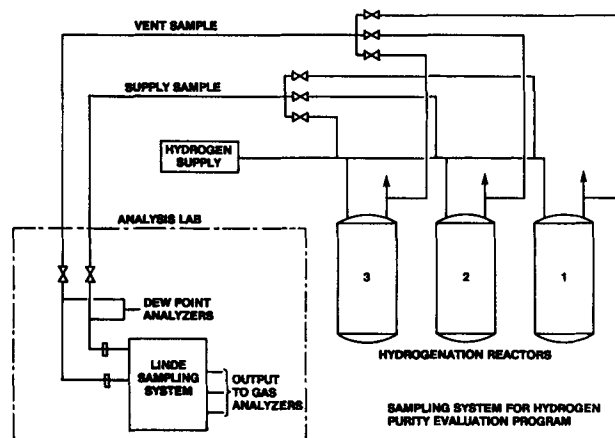


FIG. 10. Schematic of sampling system.

TABLE 1

Hydrogen Test Evaluation Parameters

Gas analysis

Hydrogen
Carbon dioxide
Carbon monoxide
Methane
Nitrogen
Water

Process

Batch time
Hydrogen usage
Solid fat index curve

TABLE 2

Headspace Gas Analysis

Component	Hydrogen supply	
	Steam reformer	High purity H ₂
H ₂	23-78%	64-97%
CH ₄	18.9-50%	0.9-11.2%
N ₂	1.2->20%	0.8-16%
CO	1000-7500 ppm	500-9000 ppm
CO ₂	90-1960 ppm	600->2000 ppm
H ₂ O	2-6.5%	1.5->7.3%

PROGRAM RESULTS

Hydrogen supply analysis. The purity of the hydrogen feed stream for all three reactors is shown in Figure 11. The hydrogen supplied with reformer showed an average purity of 96.5% with the major contained impurities being CH₄, N₂, H₂O, CO₂, and CO. The high purity supply showed less than 10 ppm of impurities.

Headspace gas analysis. The headspace gas analyses for hydrogenation reactions run with the two hydrogen feeds are shown in Table 2. The gradual build-up of inerts

HYDROGEN SUPPLY OPTIONS AND ISSUES

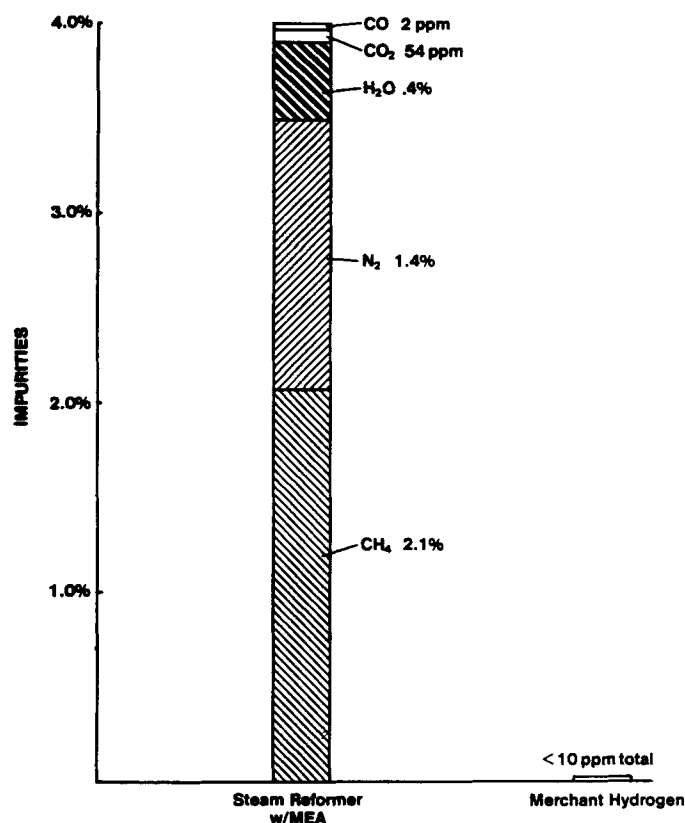


FIG. 11. Hydrogen feed contained impurities.

TABLE 3

Test Hydrogenation Products

No. 1	Frying shortening
No. 2	Soft shortening
No. 3	Hard frying stock
No. 4	Frying oil
No. 5	Fluid shortening
No. 6	Heavy duty frying stock

is obviously the result of the depletion of hydrogen by reaction, causing an increase in concentration of the components not reacting.

If the N₂ and CH₄ are used as a gauge of the inerts in the gas, the larger increase of CO, CO₂, and H₂O in the headspace indicate another source of impurities. This source is the oil. It is believed that the source of the CO and CO₂ contained in the oil was the generated inert gas that was used for blanketing and purging. The H₂O was carried over in the oil from an up-stream processing step.

Evaluation of process results. Three parameters were examined to evaluate the process results: batch time, hydrogen usage and product quality. The products that were hydrogenated during the test are shown in Table 3.

Historical batch data maintained by the client provided an excellent base of data to compare with the results with high purity hydrogen. A total of 972 batches were included in the analysis, 907 with steam reformer hydrogen and 65 with high purity hydrogen. Although the

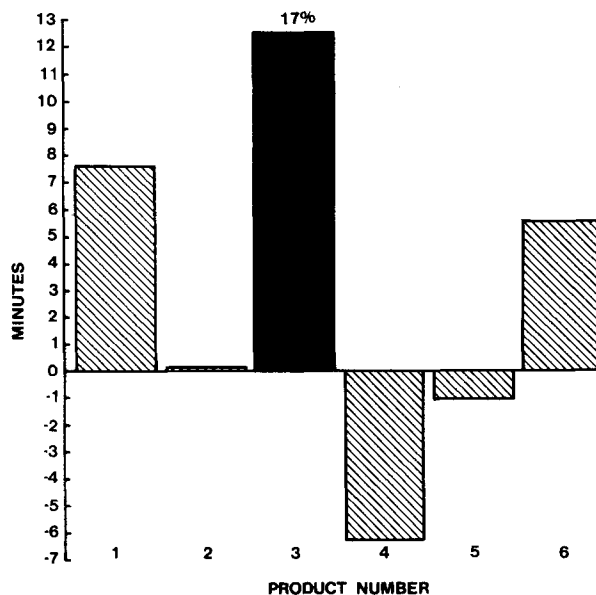


FIG. 12. Reaction time savings with high purity hydrogen.

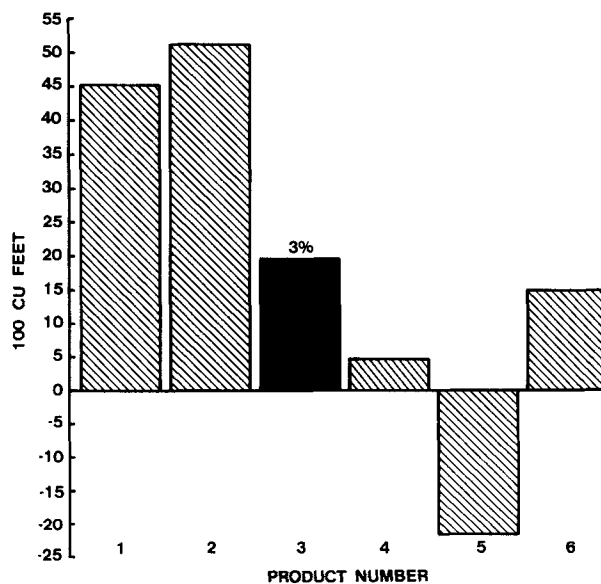


FIG. 13. Hydrogen savings with high purity hydrogen.

results for all the products run are included, the focus will be on product 3. It provided the best statistical comparison as 25 batches of it were run with high purity hydrogen. The others ran 10 batches or less, making the results less certain.

Batch time. Higher hydrogen purity contributed to a 17% reaction time savings for product 3, as shown in Figure 12. This reflects the reduction of the batch time from an average of 74.1 minutes to 61.6 minutes. Other products had a time savings up to 15%. This can be attributed to the increase in hydrogen partial pressure, both in the feed hydrogen and in the hydrogen recirculated by the recycle compressors. As CO, CO₂ and H₂O were still in the oil, the catalyst deactivating effects were not

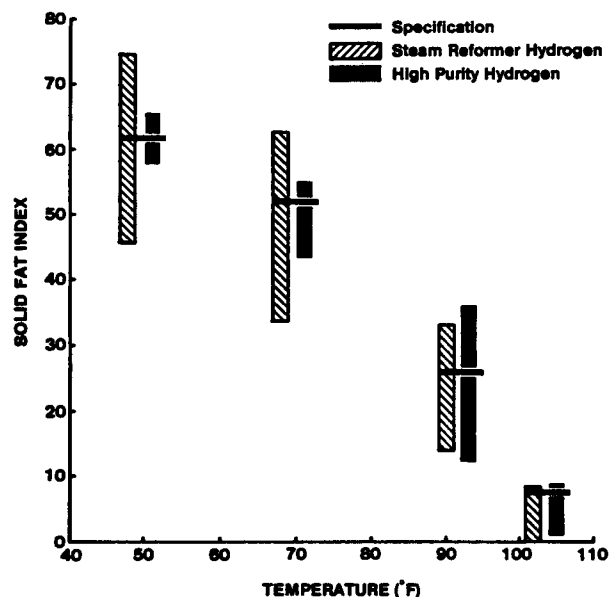


FIG. 14. Solid fat index, product number 3.

eliminated. Without these, the batch time could be further reduced. Elimination of these impurities by use of a purer purge/blanketing gas would further reduce batch time.

Hydrogen usage. As illustrated in Figure 13, less hydrogen was used with the purer hydrogen in most of the products. Savings ranged from 2% to 12% per batch. Product 3 showed a 3% savings in hydrogen.

Product quality. In hydrogenated edible oil, product quality is determined by the solid fat index (SFI) curve. Each product must meet a certain melting characteristic for each batch, or time will be wasted in formulating and blending products to meet specifications. With both hydrogen sources, the averages of the SFI at each temperature fell within specifications. The products run with high purity hydrogen were slightly harder, reflecting the faster reaction rates. In addition, with high purity hydrogen the consistency of these numbers was much greater (Fig. 14). This greater consistency results from the hydrogen purity, batch times (Fig. 15), and total hydrogen consumption.

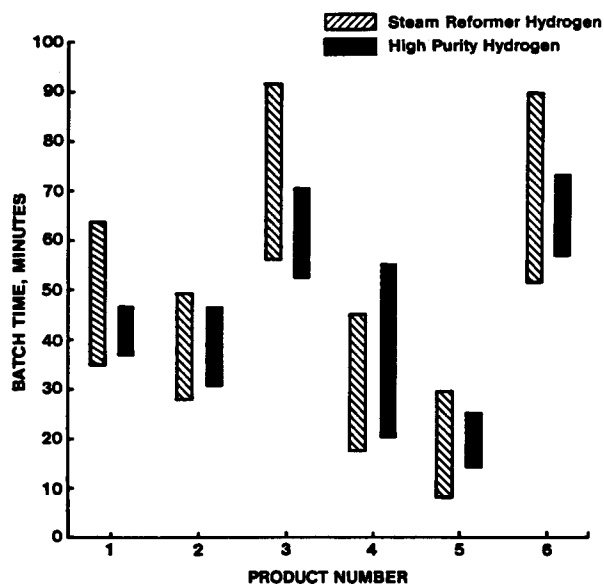


FIG. 15. Batch time.

Recommendations. In short, these results seem to suggest the two following courses of action. One, obtain a high purity hydrogen supply, whether by merchant supply or by further purifying the existing steam reformer hydrogen. This would eliminate the rapid buildup of inerts and deactivators in the recycled vent gas. Two, obtain a purer nitrogen supply to eliminate the dissolved CO and CO₂ in the oil. This would result in shorter batch times and possibly lower catalyst requirements.

REFERENCES

1. Emmett, Paul H., ed., *Catalysis, Vol. IV*, Reinhold Publishing Corporation, New York, 1956.
2. Bond, G.C., *Catalysis by Metals*, Academic Press, New York, 1962.
3. "Nickel, Copper, and Some of Their Alloys as Catalysts for the Hydrogenation of Carbon Dioxide," *Journal of ACS* 80, February 10, 1958, p. 767.

[Received January 23, 1989; accepted March 24, 1989]
[J5641]