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Activated carbon in the petroleum industry

by Dr. PAUL ZÜRCHER (Lugano)

Part II. ¹⁾

Vapor Recovery Plants

In the United States there are many plants recovering vapors from air by means of activated carbon. The petroleum industry has paid little attention to the possibilities of this method of separating the heavier hydrocarbons dissolved in gases. Oddly, the first attempts to introduce activated carbon for the recovery of natural gasoline from well gases were made in the United States. Burrell (43) failed because the necessary knowledge was not available. The idea was eagerly picked up in Europe and developed into a highly successful tool. By the Supersorbon process, one of several methods using activated carbon, four million barrels of gasoline and LPG were produced in synthesis plants in 1947 in Germany. In other countries, about two and one half million barrels annually of gasoline and LPG were recovered in Supersorbon adsorbers, mostly from natural gas. In addition, more than four million barrels of industrial solvents and benzol from coal gas were credited to this process alone (44).

Adsorption of liquefiable gases by activated carbon is very attractive because hydrocarbons of low molecular weight can exist in condensed form on an adsorbent at ordinary pressure and temperature, their vapor pressure being very low. For this reason, vapors present in concentrations as low as 0.1 lb in 1000 cuft. can be recovered. In such a case, oil absorption would require large quantities of scrubbing liquid to reduce the partial pressure of the vapors appreciably. Adsorption is much cheaper than distillation under high pressure, which requires refrigerated condensers.

The most important part of an adsorption plant is the carbon. It should have high adsorptive power; a good carbon is capable of holding 20 weight percent or more of gasoline at saturation. The adsorbate should be easily released at elevated temperature. Large particle size reduces pressure drop, and hence, power consumption. Toughness and hardness insure resistance to crumbling and lengthen the life of the adsorbent.

All types of adsorbent plants consist of three main parts: 1) one or more adsorbers containing the carbon, 2) a heat supply for desorption of the adsorbed material, 3) a condenser for the recovery of the vaporized adsorbate.

Adsorbers are either horizontal or vertical cylindrical vessels equipped with fixtures for supporting the adsorbent bed and with distributors for gas and steam. The

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thickness of the carbon bed may vary from a few inches to several feet. Provisions must be made for the quick removal of the heat of adsorption by means of cooling coils, except in small plants, where the heat of adsorption is carried off by the exit gas and dissipated by the large surface of the apparatus.

Low-pressure steam is the usual means of forcing the adsorbate from the carbon. As a rule, steam of 240 ° F. is deemed sufficient, although some condensed material remains on the carbon. Complete stripping would require steam at about 580 ° F.

The mixture of vaporized adsorbate and steam may be passed directly to a condenser followed by an automatic separator, or it may be directed through the coil inside another adsorber for the purpose of freeing the carbon of the moisture remaining after steaming.

The steamed wet carbon may be dried by heated denuded gas or by passing steam through the internal coil, or more simply by the method of the Columbia Carbon process, in which the heat of adsorption developed by a fresh charge of gas vaporizes the water left on the carbon from the previous steaming. By this procedure the temperature of the adsorbent bed is sufficiently lowered so that no further cooling is required. In other systems, the bed temperature is brought back to about atmospheric by means of cold water circulating in the internal coil or by cold denuded gas. In some plants the warm effluent gas coming from the adsorbers passes through an economizer. The heat left there by the gas serves to warm up the gas used in the drying step.

Small plants have manual controls. Larger units operate automatically. If the concentration of the adsorbable material contained in the gas remains constant, switching of the feed stream from a saturated to a regenerated adsorber as well as desorption, drying and cooling of the other adsorbers takes place by time control. If, however, the vapor content of the incoming gas changes considerably, a very sensitive vapor detector at the outlet of each adsorber will cause the switching at the moment unadsorbed vapors emerge from the carbon bed. All commercial adsorption systems are very similar. Many of the owners of the processes have patent exchange agreements.

In a double adsorption unit, a first set of adsorbers generally handles gas at 100—175 psig, while a second set receives the gas at about 90—120 psig. The first group of adsorbers contains carbon of relatively large pores and low activity; it holds back the material which is liquid at room temperature. The second group removes from the gas the compounds that are not liquid at ordinary temperature and pressure.

Among the commercial methods available, the Acticarbhone system is the most interesting to the petroleum engineer. It was developed in France for the special purpose of extracting gasoline from natural gas and has spread over the world, recovering all types of industrial solvents in addition to gasoline. The process is claimed to be extremely simple and safe in operation. Outlay for plant is considerably lower than for liquid absorption. Operating cost is substantially less, and efficiency is very high, particularly when vapor concentrations are low (5—0.09 grains per cuft.). Robinson (45) states that a properly designed Acticarbhone plant can produce such large savings that it will pay for itself within a period of six months to two years. Labor requirements are negligible in fully automatic plants. Yields of 97—99 % are said to be possible.

There is no limit to the size of a unit. Gasoline plants have at least four adsorbers; in larger installations there may be as many as eight, and one has twelve. With four adsorbers in a plant, two are on stream reaching saturation at different times; one is being desorbed, and the fourth is in the cooling stage.

Information on operating costs generally refers to the adsorption of solvents from

air. A process comparable with gasoline is that of the recovery of benzol from coal gas or coke oven gas (46). The concentration of the benzol in the gas is similar to that of natural gasoline in well gases, and the molecular weights and boiling points are within the same range. Especially interesting is Howell's (46) comparison of the carbon adsorption process with the oil absorption. The carbon recovered 3,93 gallons of benzol per ton of coal, oil absorption yielded 1,67 gallons.

Detailed cost figures of a small European plant have recently been received (44). A unit of the Supersorbon type collects four metric tons of gasoline and four tons of LPG daily from a synthesis plant. For comparison with American conditions, weights have been converted into gallons, assuming an average API gravity of the liquids of 82 degrees. A German Mark is taken at 25 cents.

Recovery of about 3200 gallons daily of Natural Gasoline and LPG from a Gasoline Synthesis Plant.

1) Exhaust steam, 20 psig (85 cents per 1000 lb)	\$ 75.00
44 tons daily	
Steam at 367 psig (\$ 1.42 per 1000 lb)	12.50
4.4 tons daily	
Circulating cooling water (1320 tons daily)	
Replacing evaporation (34 cents per 1000 gal.)	3.25
39.6 tons daily	
Cost of pumping	6.00
Electricity, 800 kwhr daily (2.75 cents a kwhr)	22.00
Labor, 1 man, 1 helper, 3 shifts	15.00
General supervision	7.50
Consumption of carbon, less than 2 lb per ton at 34 cents a lb	6.00
	<hr/>
	\$ 147.25

Cost per gallon: 4.6 cents

2) Compression and Loading of 1600 gal. LPG	
2400 kwhr daily	\$ 58.50
Pumping 39 600 gal. cooling water	0.75
Makeup cooling water, 1320 gal.	0.50
Labor, 1 man 3 shifts	7.50
General and supervision	3.75
	<hr/>
	\$ 71.00

Cost of compression of 1 gallon 4.4 cents.

Amortization and interest on the invested capital is calculated at 15 % per year. Including licence fees, the total cost per gallon of gasoline amounts to 7.0 cents and of LPG to 12.6 cents. At prices prevailing in Germany, a profit of \$ 187 000 per year is figured on an investment of \$ 155 000. Gasoline is worth 27.2 cents a gallon before tax, and LPG 32.6 cents.

This estimate permits to make a very rough guess about the possibilities of a carbon adsorption plant in natural gas service in the United States. The cost of most of the utilities in Germany is much higher than that prevailing in the American petroleum industry. Reducing these items to American standard values and assuming automatic control, which would cut labor cost, but taking into account the much higher wages, and doubling the cost of supervision, a gallon of gasoline would come to about 2.5 cents, and a gallon of LPG to 7 cents before investment charges. Doubling the invested capital, charging 15 % for amortization and interest, the total cost per

gallon would be 4.2 cents for gasoline and 7.8 cents for LPG for the plant producing 3200 gallons daily. Such a small unit would hardly fit into the American picture. A large plant might realize at least a fraction of the profits claimed by European engineers.

Liquid extraction Processes

The difficulties encountered in applying a moving bed for liquid-phase separation by adsorption are explained by Mair and Forziati (47). Large adsorbent particles are required in order to reduce pressure drop and prevent the lifting of the adsorbent. But diffusion of the liquid through large granules is slow, time of contact must be long. An adsorbent of small grain size acts more rapidly and would be preferable. The process of the California Research Corporation (48) uses a very finely divided adsorbent and imitates countercurrent operation by dividing the adsorbent bed into a number of sections that are switched into and out of the cycle as needed. The operation is divided into four zones; 1) for raffinate refining, 2) for extract enriching, 3) for stripping, 4) for cooling. In the plant described there are nine columns charged with adsorbent. The charge enters column 4 (Fig. 10) together with the effluent from column 3 of the extract enrichment zone. In columns 4 and 5, the charge loses its extract to the adsorbent and displaces any desorbent left from the previous stripping operation. The effluent goes to the raffinate still. Columns 8 and 9 are being stripped of extract (aromatics) with hot desorbent. The first part of the discharge is pumped as recycle to the extract enrichment zone, and the balance to the extract still. Columns 6 and 7, which have been stripped, are being cooled by cold desorbent. At switching time, all columns will move a step forward against the liquid stream. Column 1 will take the place of column 9 in the stripping zone; columns 2, 3 and 4 will comprise the extract enriching zone, while columns 5 and 6 will form the raffinate enriching zone.

Saturated paraffinic hydrocarbons, e. g. pentane, hexane, heptane, iso-octane, kerosine, are suitable desorbents. They dissolve the adsorbate, are taken up slightly by the adsorbent and are very easily separated from the products.

The plant is usually operated at atmospheric temperature in the raffinate refining and enriching zones and at higher temperatures in the stripping zone. Cycle time is from 0.25 to two hours, and liquid velocities are 100—1000 gallons per hour per square foot of horizontal area.

The process has been developed for the practically quantitative separation of high-purity aromatics from petroleum fractions of wide boiling range. Operating costs for a plant of 2000—15 000 barrel daily capacity is estimated at 1—3 cents a gallon of charge. The aromatics produced will cost about 6 cents a gallon. Claims made in favor of this development of the California Research Corporation are: wide flexibility, production of many chemical intermediates from complex charge stocks, yields and purity of products considerably higher than those from conventional solvent extraction processer or acid treating, no loss of material. It is further stated that the use of small adsorbent sizes in fixed beds permits operation in smaller adsorption units at higher liquid velocities and at lower adsorbent replacement than for moving bed plants. Automatic cycling operation and optimum inter-zone recycling reduce to a minimum the quantity of adsorbent needed and the amount of stripping liquid as well as the distilling and the heat required.

A different procedure of separating aromatics from petroleum fractions is based on the method applied by Rossini and coworkers in their research. The Sun Oil Company which developed the Arosorb process, is building a plant of a daily charge capacity of 10 000 barrels of Houdriformer product (49). About 900 bbl. of benzene

or toluene and 1000 bbl. of xylenes will be made per day. The aromatic constituents of the charge are retained by the adsorbent. A butane wash removes the saturated compounds left in the tower at the saturation point of the adsorbent. By means of a mixture of xylenes the aromatics are stripped. The components in the effluent change gradually. As the content of aromatics in the effluent begins to increase, the stream is automatically switched to aromatic storage. Control is by the change in refractive index of the discharge.

Depending on the desired purity of the products and on the composition of the charge and other factors, the investment cost for a plant of 1000 bbl. of aromatic products per day is estimated at \$ 1 200 000, and for 2 000 bbl. at \$ 1 900 000. Operating cost per gallon of aromatics is estimated at 6½ cents for the smaller and at 6 cents for the larger plant.

Comparison of the process of the California Research Corporation with that of the Sun Oil Company will discover many similarities. The interesting difference is that the California process uses only one desorbent with application of heat, while in the Sun Oil process one liquid removes the adherent saturated compounds from the adsorbent bed before another solvent desorbs the aromatics from the adsorbent. Two solvents require more tanks and more distillation equipment than is necessary when only one solvent does the job. Yields and quality of the products from the two processes are comparable, and calculated costs per gallon of aromatic products is stated to be 6½ to 5 cents, depending on the size of the plant of the Sun Oil Arosorb process, and 6 cents for pure aromatics turned out by the plants of the California Research Corporation.

While the two developments are originally based on silica gel, their principles can

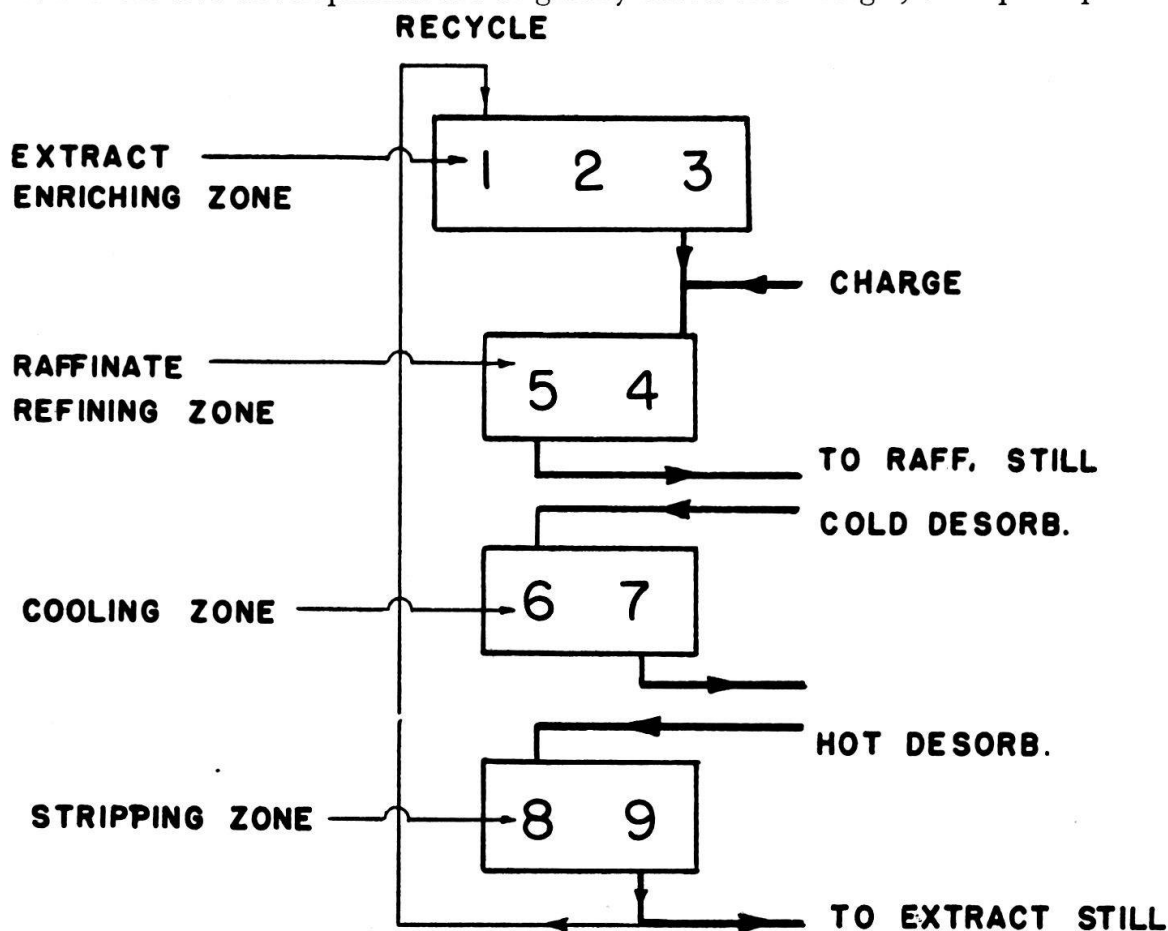


Fig. 10 Flow Chart of California Research Corporation

be transferred with modifications to plants where activated carbon is the adsorbent. They have been mentioned here as steps in the evolution of adsorption technique.

Continuous countercurrent processes with moving bed

While the petroleum refiner is certainly interested in the recovery of liquefiable compounds from gases by adsorption, his main desire is to have an economical means for the separation of small amounts of valuable components from complex mixtures when the oil absorption process is inapplicable. Other industries, depending on the quantities of vapors to be recovered, resort either to batch or to cyclic processes. In order to meet the demand of the refiner for the treatment of large quantities of gases, these plants would require much capital and huge amounts of adsorbents. For this reason, several approaches to continuous countercurrent treatment have been suggested. Wilson and Lamb (50) designed an adsorber in which the solid material slides downward in zig-zag fashion against rising vapors. Another idea by Wilson is to move a wire-mesh belt through a horizontal air-tight cylinder. Granular adsorbent drops onto the belt at one end and leaves at the other end. Vapors to be recovered rise vertically through the moving adsorbent bed. In these devices the solid material is stripped of the adsorbed vapors in a separate vessel.

The Hypersorption process solved the problem in an elegant fashion. The first unit was built for a chemical company and was based on the experience gathered in a pilot plant of the Union Oil Company of California and was engineered by the Foster-Wheeler Corporation. (51). Essential parts of a Hypersorption unit are (Fig. 12) a tower containing two heat exchangers, a cooler at the top and a Dowtherm stripper at the bottom. Between these exchangers are the adsorption and the

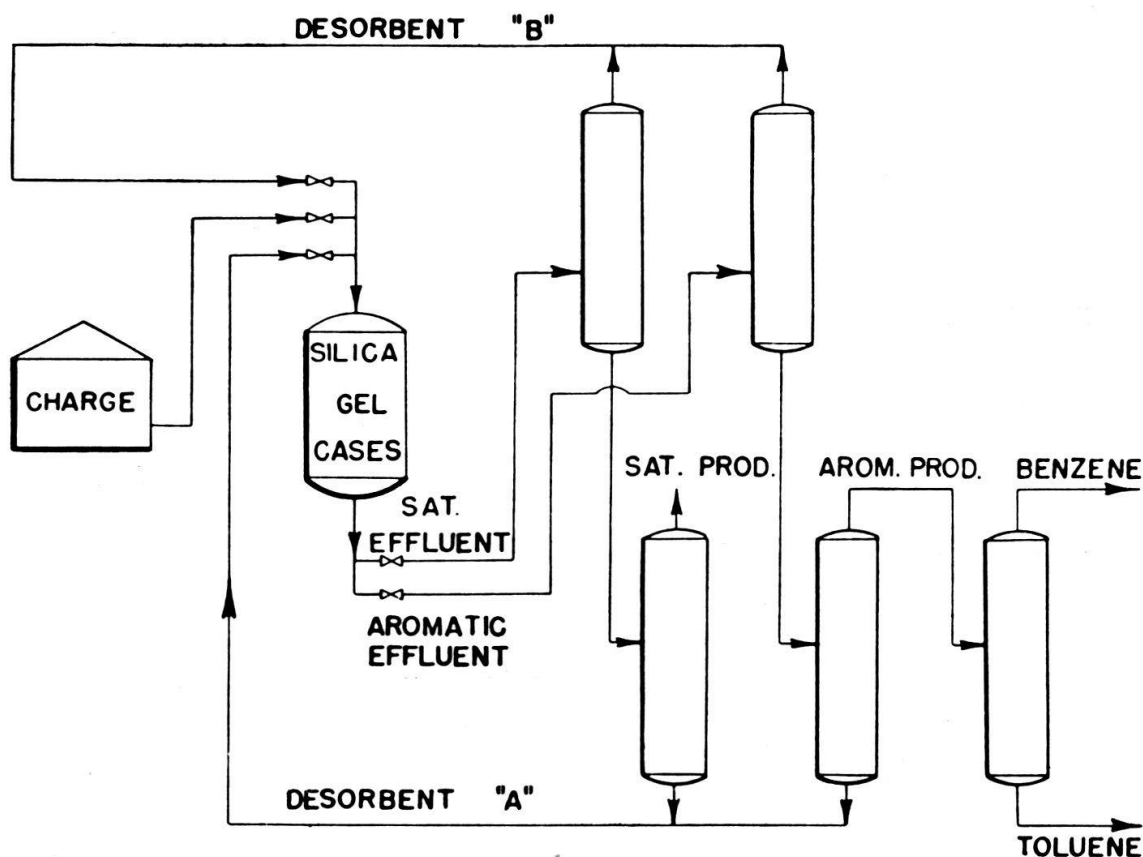


Fig. 11 Flow Diagram for the Arosorb Process (Courtesy Petroleum Refiner)

rectifying sections with trays for the introduction and withdrawal of gas streams. Typical of a unit is a gas lift for returning of the stripped adsorbent to the top of the column. A reactivator is provided for the purpose of regenerating the activated carbon contaminated with diolefins and heavier hydrocarbons.

The carbon falling from a hopper through the cooler at the top of the column meets with the stream of the feed gas and adsorbs the heavier components. The gases of lower molecular weight escape at the top of the column. In its downward path, the carbon reaches the heating zone at the bottom, where the adsorbate is released. For complete stripping, steam is introduced into the bed below the heating section and passes upward through the heating tube bundle countercurrent to the carbon. Steam and desorbed bottoms products are taken off as a side-stream at a tray. They are cooled, separated, and the hydrocarbon gas is dried by alumina.

A part of the stripped heavier hydrocarbons moves upward in the descending carbon bed and produces a sharp separation of the lighter from the heavier gases by reflux.

The flow of the carbon through the column is controlled by a mechanical discharge device below the stripper. A gas lift returns the hot adsorbent to a hopper at the top of the tower. The carbon, at a temperature of about 400° F., travels downward in the column through the tube and shell water cooler, where its temperature is reduced to 120° F. A small portion of the overhead discharge gas passes upward through the cooler and dries the adsorbent.

Details of the commercial unit were published in 1948 (52). This plant treats on the average 1.8 million std. cuft. of gas daily under a pressure of 75 psig. A product gas of 92 % ethylene content with less than 0.1 % methane is separated from the charge which consists of hydrogen, methane, and 4.5—6% ethylene. The overhead product is a mixture of hydrogen and methane with less than 0.1 % ethylene.

The tower is 4.5 feet in diameter and 85 feet high.

Fifteen thousand pounds of activated carbon are circulated in the unit at the rate of 18 000 pounds an hour. Originally, the adsorbent was made from apricot pits. The dust formed by disintegration amounted to 100 pounds daily and was removed by the cyclones. Replacement cost was \$ 5.00. A change to coconut shell carbon has reduced this loss by 90 % or to one thousandth of one percent per cycle.

Since first announced, the process has been refined and adapted to a number of operations, and the capacity of the units has been increased to 16 million cuft. per stream day. There are now six hypersorption plants in operation, five of them in the petrochemical industry.

A few examples will show what Hypersorption can accomplish. At the original plant of the Dow Company, where about 76 000 cuft. of gas were treated per hour, the composition of the charge, the product, and the overhead gases was as follows:

	Feed Gas vol. %	Product Gas vol. %	Overhead Gas vol. %
Hydrogen	37.2	—	32.3
Nitrogen	1.5	—	1.3
Carbon monoxide	1.0	—	1.0
Oxygen	0.2	—	0.2
Methane	53.2	0.1	62.5
Carbon dioxide	0.2	2.9	—
Acetylene	0.2	2.9	—
Ethylene	6.4	92.6	—
Ethane	0.1	1.5	—

Ethylene can similarly be recovered from refinery gas streams (53). A feed gas containing 5.8 mole percent ethylene yielded a bottoms product of 92.7 mole percent ethylene, the overhead product consisting essentially of one third hydrogen and two thirds methane.

Hypersorption is employed in the separation of propane and butanes from natural gas (54). Concentrations of as low as one and one half percent propane are recovered with a yield of 98 percent of propane and heavier compounds.

Propane Recovery by Hypersorption from Natural Gas

Composition	Feed mole %	Overhead Product mole %	Propane Side Cut mole %	Bottom Product mole %
Methane	78.1	81.5	—	—
Ethane	13.4	18.3	0.4	—
Propane	6.9	0.2	96.4	0.8
Butane	1.3	—	2.9	81.1
C ₅	0.3	—	0.3	18.1
	100.0	100.0	100.0	100.0

In this operation, three product streams are made. The propane is a side cut in the rectifying section (Fig. 12). Rectification is accomplished by means of carbon coming directly from the top of the unit without getting into contact with the gas stream rising above the rectifying section of the column. In this manner a Hypersorber can replace the absorber, the stripper, the deethanizer, and the depropanizer of an absorption unit. A plant for treating 60 million cuft. of gas daily would work at 325 psig and would have a tower 10.2 feet in diameter and 146 feet high, charged with 68 tons of activated carbon.

Refinery gases can be split by the Hypersorber into fractions of C₁, C₂ and C₃. If the ethane is to be cracked for the production of ethylene, the side cut containing 99 percent or more of ethane and ethylene is fractionated in a small low-temperature column, in which the overhead is ethylene of 97 percent concentration or higher. The propane can be used as fuel or as raw material for petrochemicals (53).

Recovery of Ethylene from a Refinery Gas Stream by Means of Hypersorption

Composition	Hyper Feed Mole %	Overhead Product Mole %	Bottoms Product Mole %	Hyper Side Cut Mole %	Ethyl Fraction Overhead Mole %
Hydrogen	11.91	25.40	—	—	—
Methane	35.46	73.92	—	0.54	1.35
Ethylene	13.24	0.35	1.79	39.32	97.11
Ethane	25.18	0.33	3.44	59.84	1.54
Propylene	4.42	—	29.35	0.16	—
Propane	8.32	—	54.30	0.14	—
C ₄	1.47	—	11.12	—	—
	100.00	100.00	100.00	100.00	100.00

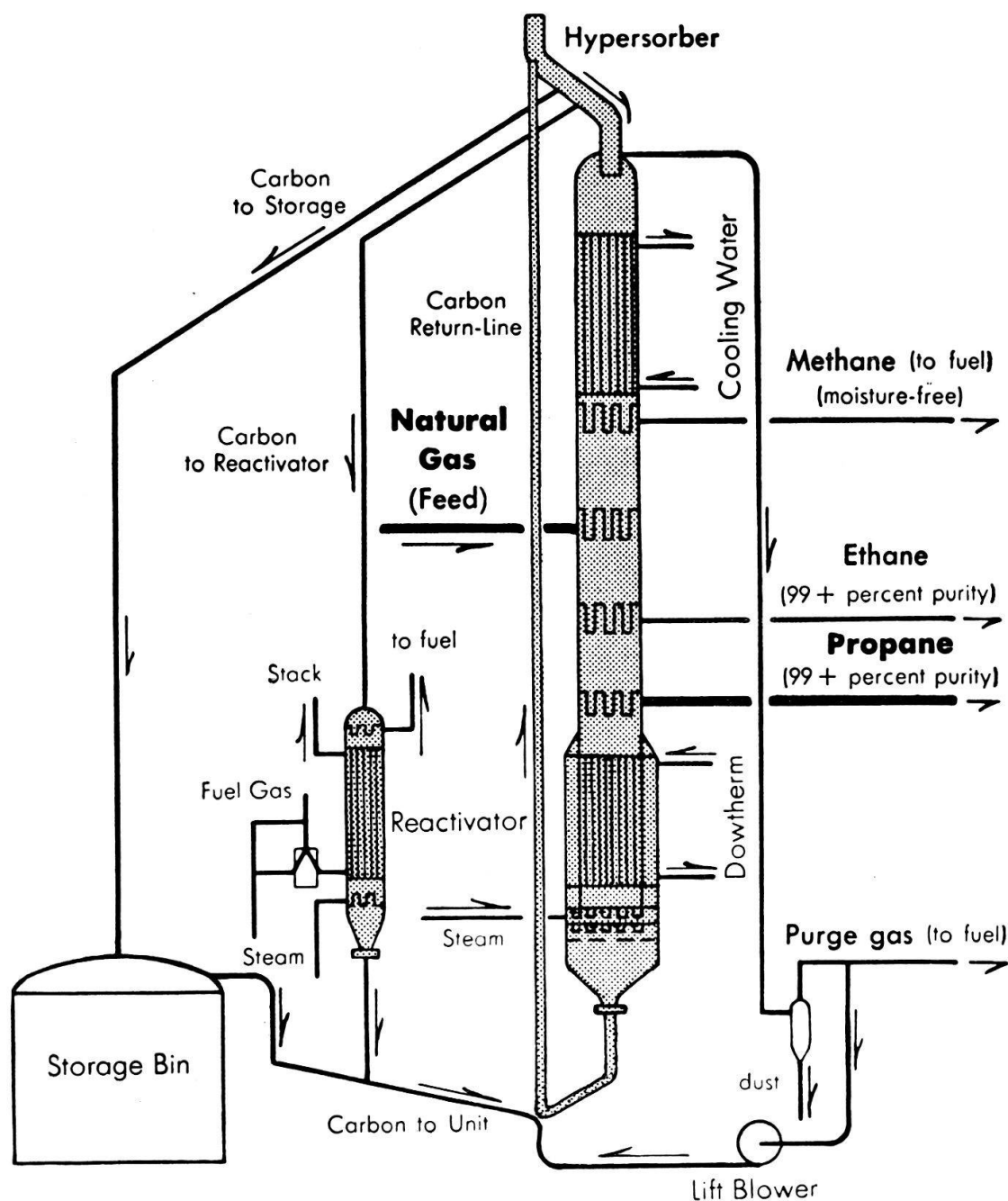


Fig. 12 Flow Diagram of Hypersorption Process when operating on natural gas to recover ethane, propane and other hydrocarbons (Courtesy Oil and Gas Journal)

Another promising application of the Hypersorber is the separation of nitrogen from natural gas for the purpose of increasing the heat content of the fuel. In a three-product unit, an overhead product of methane and nitrogen, a side cut of ethane, and a bottoms of propane and heavier are made. The overhead cut is treated in a second unit, where nitrogen of 99 percent purity is taken off as overhead, and methane of about the same concentration is the bottoms product. The ethane from the first unit is combined with the methane from the second unit to give a nitrogen-free gas. It is claimed that capital required and utilities consumed are very low.

The Hypersorption units operating in the petrochemical industry separate ethylene from synthesis gas. In a chemical plant near Houston, pure methane is made from natural gas. Together with ammonia and air, methane is the raw material for the

production of hydrocyanic acid del. Acetylene from partial combustion of natural gas is concentrated in the bottoms product of a Hypersorber to a purity of 83 percent, most of the balance being carbon dioxide.

Further possibilities are the treatment of synthesis gas for the removal of methane, the separation of hydrogen sulfide and hydrocarbon gases from hydrogen in hydroforming. Hydrogen chloride, a by-product of chlorination of hydrocarbons can be recovered as a bottoms product of 99.8 percent purity.

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