STATEMENT OF PROBLEM

A. I. Ch. E. STUDENT CONTEST PROBLEM FOR 1947

Prepared by Mott Souders, Jr., Chairman
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To the Contestant:

The committee has selected a problem which typifies the principal economic function of the chemical engineer. From the first assessment of a new idea to the final design of a plant, the engineer is confronted with a series of economic choices and the ultimate validity of those choices is an important factor in the economic survival of the industrial unit to which the engineer is attached.

The problem this year is a preliminary evaluation of three methods for recovering hydrogen from a gas with the objective of deciding which is economically preferred. As presented, this problem is a simplification of an actual evaluation made several years ago. In developing the student problem, internal choices within each process have been reduced to a minimum by making the stated conditions of operation as rigorous as possible. There still remain, however a number of internal variations from which you will need to make an optimum selection. In making such selections, it is well to remember that variations which will have small effect on over-all cost are unimportant. Since this is a preliminary evaluation far ahead of any projected installation, details of instrumentation, piping or construction are superfluous. It is necessary, however, to foresee possible difficulties in ultimate operation and to provide equipment to overcome them.

The following memorandum and supplementary information complete your instructions for the problem.

TO: J. DOE, PROCESS EVALUATION ENGINEER
FROM: J. SMITH, CHIEF ENGINEER
SUBJECT: COST OF RECOVERING HYDROGEN

Our Market Development Department is considering several hydrogenation processes and has asked us to estimate the cost of recovering hydrogen of 95% purity from 10 million standard cubic feet per day of gaseous feed (standard = 32°F, 1 atm.), available at 100°F. and 20 lb./sq. in. abs. and containing 72.5% H_2, 2.5% C_2H_6 (mol per cent). At least 80% of the hydrogen in the feed must be recovered and the recovered hydrogen must be delivered at a pressure not less than 375 lb. per sq. in. absolute. The residual gas is to be used as fuel and may be delivered at any convenient pressure above 20 lb. per sq. in. absolute. The feed gas has fuel value. Processes based on water-gas reaction, pyrolysis of hydrocarbons, and low temperature separation have already been investigated, but three other processes have been suggested as having possible application.

(a) Oil absorption at ordinary temperatures.

(b) Selective adsorption on activated charcoal.

(c) Gaseous diffusion through a porous membrane.

Your report will be used to determine: (A) whether any of these processes offers possibility of producing hydrogen at a cost competitive with other methods, i.e., at less than 35 cents per 1,000 cu. ft., and (B) which one of these processes is the most promising for further research and development. Since these evaluations will necessarily be preliminary, a complete economic study of each process will not be required. It is not necessary to complete the calculations for all three processes if you can show by preliminary evaluation that one or two of them are relatively unfavorable. In your report, therefore, I should like your conclusion as to which process is most promising together with the reasons for your choice and the minimum of calculated data required to support the conclusion, as well as a detailed cost estimate for the best of the three processes supported by a flow sheet showing operating conditions, heat and material balances, and sizes of major equipment.

Descriptions of the three processes and essential engineering data are given in the supplementary information attached.

Oil Absorption

The essential features of this process are compression of feed, absorption of predominantly heavier components by a lean hydrocarbon oil in a bubble-plate column, flashing of the fat oil to remove absorbed components, and recycling of the stripped oil to the absorption column.

As a compromise between amount of lean oil circulated and lean oil loss during absorption and stripping, we suggest that you use a $C_7 - C_9$ fraction available in our plant. This fraction may be assumed to be equivalent to n-octane, and is available at 6.5 ¢/gal.

Refrigeration is not to be employed in this process and since cooling water is available at 85°F and minimum temperature approaches of 15° in exchangers are acceptable, the gas feed after compression can be cooled to a minimum temperature of 100°F. The heat of absorption and heat of vaporization of the absorbed components may be assumed to be negligible because of the obviously high oil/gas ratio which will be required.

Since the hydrogen is to be delivered at a minimum pressure of 375 lb. per sq. in., it is a reasonable assumption that the absorption inlet pressure can be fixed at 400 lb. per sq. in. without further consideration.

The absorbed gas must be stripped from the fat oil without excessive loss of absorption oil and also at conditions that are consistent with the minimum specifications for 80% recovery and 95% purity of hydrogen. An isothermal flash of the fat oil with vapor in equilibrium with residual liquid will probably be adequate, flashing at an optimum pressure to be determined. See Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill, 1944, p. 597 - 603 for solution of flash problems.

Heat contents are given in Table 1, vapor-liquid equilibrium data in Table 2, and molar volumes of liquids in Table 3.

Experience has indicated that bubble-plate columns should be designed with plates at not less than 18 inch spacing, a liquid weir head of not over 2-1/2 inches, and a weir angle of not more than 135°. The recommended maximum gas and liquid rates for these conditions are given in Table 4. An over-all plate efficiency of 30% can be assumed for these conditions.

The cost of absorption oil added as makeup should be credited for the net heating value of octanes in the flashed methane-ethane stream, using a fuel value of 20 ¢/million BTU.

Selective Adsorption

The adsorption process, using activated charcoal, is to be considered for cyclic operation of fixed charcoal beds, with desorption of each bed by flashing to 20 lb. per sq. in. after saturation at 400 lb. per sq. in. absolute pressure, followed by a periodic regeneration with hot flue gas plus an air purge to cool to 100°F.

Our research laboratory has obtained adsorption data for several hydrogen-methane mixtures on a charcoal sample, Number 276-A, at 100-120°F, and various adsorption pressures; these data are given in Table 5. Charcoal 276-A has a bulk density of 0.45 gm./cc., and the percentage dead space (random packing) was found to be 75%. The small amount of ethane in our feed can be assumed to be adsorbed as methane. The laboratory tests indicated that equilibrium adsorption is nearly instantaneous.

An adsorption-desorption-regeneration cycle using at least three fixed beds is recommended, with an eight hour regeneration, including purging, of each bed every 24 hours. While one bed is being regenerated, the two free beds are on 30 minute adsorption and 30 minute depressuring cycles. The percentage of hydrogen in the lean gas during the adsorption period may be taken to be 97%. Regeneration will include 25 standard cu. ft. of flue gas per lb. charcoal in the bed and 75 standard cu. ft. of air per lb. charcoal; flue gas at 600°F and 5 lb. per sq. in. gage and air at 90°F and 5 lb. per sq. in. gage are available at a pro-rated cost from other sources. The time cycle for the process is tabulated below.

TIME CYCLE
FIXED BED CHARCOAL ADSORBER

Time, Hours:	0 - 8	8 - 16	16 - 24
Adsorption and Desorption	Beds 1 and 2 alternating on 30 min. cycles	Beds 3 and 2 alternating on 30 min. cycles	Beds 1 and 3 alternating on 30 min. cycles
Regeneration and Purge	Bed 3	Bed 1	Bed 2

Gas holders should provide 30 minute residence time for the hydrogen product at adsorber pressure, and 30 minute residence time for the desorbed gas at 20 lb. per sq. in. absolute pressure. The regeneration flue gas and air will be vented. The annual make-up of charcoal can be assumed to be 15% of the initial charge.

Gas velocities in the adsorbers should not exceed one ft. per sec. calculated on the cross-section of the empty vessel.

Gaseous Diffusion

Our New Processes laboratory has reported that an appreciable separation of hydrogen and methane is obtained when mixtures of the two are diffused through porous membranes; for a given gas system and at a constant temperature the enrichment per diffusion was found to be a function of the feed composition, viscosity and pressure, pressure drop across the membrane, fraction of feed diffused, and pore diameter and length. Several membranes have been compared at a feed temperature of 100°F, and the following equations represent the separation obtained at 100°F with the most efficient membrane investigated (designated hereinafter as Number 297-M):

$$N_1 = 0.1 \frac{\Delta p_1}{\sqrt{M_1}} \ln_e \frac{N_f}{N} + 0.000003 \frac{\Delta P}{\mu_f} X_{B_1} P_{ave} \qquad (1)$$

$$N_2 = 0.1 \frac{\Delta p_2}{\sqrt{M_2}} \ln_e \frac{N_f}{N} + 0.000003 \frac{\Delta P}{\mu_f} X_{B_2} P_{ave} \qquad (2)$$

$$\Delta p_1 = P_B X_{B_1} - P_D X_{D_1} \qquad N = N_1 + N_2$$

$$\Delta p_2 = P_B X_{B_2} - P_D X_{D_2} \qquad \frac{N_1}{N} = X_{D_1}$$

$$\Delta P = P_B - P_D \qquad \frac{N_2}{N} = X_{D_2}$$

$$P_{ave} = \frac{P_B + P_D}{2} \qquad \alpha_{12} = \frac{X_{D_1}}{X_{D_2}} \quad \frac{X_{B_2}}{X_{B_1}}$$

where:

N = Total flow of both components through the barrier, cu. ft. (at 32°F, 1 atm.)/hr./sq. ft. of membrane cross-section.

P = Pressure, lb./sq. in.

M = Molecular weight.

N/N_f = Volume fraction of feed diffusing.

μ_f = Viscosity of feed gas, centipoises.

X = mol fraction of a component.

α = Separation factor.

Subscripts:

1,2 = Refer to components 1 and 2.

B = Refers to reject stream.

D = Refers to diffusate stream.

The last terms of Equations (1) and (2) account for the non-selective flow through the barrier and it is apparent that the value of these terms should be small relative to the first terms, if efficient separation is to be obtained.

It will be evident that more than one diffusion stage will be required to go from a feed concentration of 72.5% H_2 to a hydrogen purity of 95%. It appears that the best arrangement is a battery of stages in series, diffusing through each stage one-half of the feed to that stage, and recycling the amount not diffused (reject) back to a previous stage. Concentrated hydrogen is removed from the top stage, feed gas is added to the stage wherein the composition most nearly matches the feed composition, and a reject stream is withdrawn from the bottom stage.

A schematic drawing of this cascade arrangement of stages is shown in Figure 1. The maximum volume of gas fed to, and diffused through, a stage occurs at some intermediate stage; this intermediate stage of maximum size is close to but not necessarily adjacent to the feed inlet. A constant pressure drop per stage is recommended, with recompression at each stage.

Preliminary tests indicate that the membrane, No. 297-M, can withstand a pressure drop of 15 lb. per sq. in. if correctly supported in a large installation. It is suggested, therefore, that you use the following conditions as the basis of your calculations for each stage:

P_B = Discharge pressure = 20 PSIA.
P_D = Suction pressure = 5 PSIA.
Diffusion temperature = 100°F.
Fraction of feed diffused = 0.50.
C_2H_6 Content of feed, assume equivalent to methane.

Pressure drop in lines, etc., may be neglected, so that $P_B - P_D$ becomes equal to the pressure drop across the membrane. Your evaluation will require a stage-by-stage calculation involving a trial solution of Equations (1) and (2) as well as a material balance around each stage. Beginning at either end of the cascade, it may be necessary to change slightly the fraction of feed diffusing in one or more stages beyond the feed stage, in order to balance both composition and volume of the exit stream at the other end of the cascade. The membrane area for each stage may be computed from the volume flow and the summation of the correct values of N_1 and N_2.

Compressors and Pumps

Compression for the three separation methods may be calculated as an adiabatic process, using the ideal gas laws and a molal average value for the ratio of specific heats (H_2 1.4, CH_4 1.3, C_2H_6 1.2). The compression ratio per stage should not exceed 5 to 1. Gas-engine drive will be used for all compressors with an over-all efficiency of 0.15 (i.e., 15%) where efficiency is defined as the ratio of theoretical work of the cycle to net heat in the fuel.

All pumps will be centrifugal and driven by electric motors. For these, an over-all efficiency of 0.75 (i.e., 75%) may be assumed where efficiency is defined as the ratio of work against the head to energy input to the motor.

Cost Estimates

The costs of equipment and utilities, on a unit basis, are given in Table 6. The total plant cost, which will include installation, piping, instrumentation, etc., may be taken as three times the equipment costs. The total capital investment will include costs of plant and inventory of process materials.

The processing cost may be computed as cents per 1,000 standard cu. ft. of

95% hydrogen. This should include 5 year amortization of the capital investment, operating costs, and net feed cost.

The operating costs for each process include:

Fixed expenses, 10% of plant cost per year.

Repairs and maintenance, 5% of plant cost per year.

Labor and supervision, $27,000 per year.

Utilities, fuel, steam, power, etc.,

Losses of process materials, absorption oil, charcoal.

An operating time of 350 days per year may be assumed.

TABLE 1

VAPOR HEAT CONTENTS, BTU/LB MOLE

Base: Zero Heat Content of Vapor at 0 Pressure and 0°Rankine

Press. PSIA	20				200			400		
Temp., °F.	H_2	CH_4	C_2H_6	C_8H_{18}	H_2	CH_4	C_2H_6	H_2	CH_4	C_2H_6
50	3,453	4,071	4,765	12,105	3,449	3,984	4,323	3,436	3,876	3,555
100	3,799	4,498	5,398	14,616	3,794	4,429	5,050	3,781	4,337	4,593
200	4,493	5,395	6,779	19,934	4,487	5,344	6,566	4,475	5,275	6,194
300	5,190	6,364	8,329	25,274	5,184	6,320	8,171	5,172	6,267	7,981

LIQUID HEAT CONTENTS, BTU/LB MOLE

		HEAT CONTENT OF DISSOLVED COMPONENTS								
		20 PSIA			200 PSIA			400 PSIA		
Temp. °F.	C_8H_{18}	H_2	CH_4	C_2H_6	H_2	CH_4	C_2H_6	H_2	CH_4	C_2H_6
50	-5,363			-315	5,257	3,788	155	5,637	2,186	835
100	-2,322			310	5,802	3,727	780	5,982	2,712	1,930
200	4,286			1,683	6,596	5,079	3,543	6,676	4,407	3,943
300	11,590			3,233	7,293	7,864	5,093	7,373	6,374	5,853

TABLE 2

K VALUES FOR HYDROGEN, METHANE, AND ETHANE IN OCTANE

$$K = \frac{\text{mole fraction in vapor}}{\text{mole fraction in liquid}}, \text{ at equilibrium.}$$

Press. PSIA	HYDROGEN			METHANE			ETHANE		
	Temperature			Temperature			Temperature		
	75°F.	100°F.	150°F.	95°F.	100°F.	150°F.	75°F.	100°F.	150°F.
15	1,360	1,270	1,070		233			34.5	
20	1,020	950	800		175		23.0	28.8	41.0
25	816	760	640		140		18.5	23.0	33.0
50	408	380	320	69	70	76	9.1	11.4	16.2
100	204	190	160	34	35	38	4.75	5.95	8.3
200	102	95	80	17.2	17.5	19	2.54	3.10	4.36
400	51	47.5	40	8.3	8.8	10.3	1.36	1.70	2.33
500	42	38	33	6.7	7.0	8.1	1.13	1.38	1.88

TABLE 2
(Continued)

K VALUES FOR OCTANE IN HYDROGEN VAPOR

Press. PSIA	75°F.	100°F.	150°F.
15	0.060	0.117	0.33
20	.045	.087	.25
25	.036	.070	.20
50	.018	.035	.100
100	.0090	.0175	.050
200	.0046	.0086	.025
400	.0023	.0049	.014
500	.0020	.0040	.0115

TABLE 3

MOLAR VOLUME OF LIQUID n-OCTANE AT 100°F.

Pressure lb./sq.in. absolute	Cu. Ft./Lb. Mole Octane	Octane plus 1% M CH_4 or 1% M C_2H_6
50	2.659	
100	2.657	2.629
200	2.655	2.627
400	2.647	2.619
500	2.643	2.615

TABLE 4

LIMITING VAPOR VELOCITY IN BUBBLE-PLATE COLUMNS

18 IN. PLATE SPACING

d_L, d_V = density of liquid and vapor at point of maximum vapor flow.

U = allowable vapor velocity based on column cross-section, ft./sec.

$\frac{d_L}{d_V} - 1$	U
30	0.38
100	.70
300	1.2
1,000	2.2
3,000	3.8

LIQUID CAPACITY OF BUBBLE-PLATE COLUMNS

WEIR ANGLE = 135°
LIQUID HEAD ABOVE WEIR = 2.5"

Liquid, GPM	Column Diameter, Feet
500	4.0
750	6.0
1,000	8.0
1,500	12.0
2,000	16.0

TABLE 5

HYDROGEN-METHANE ADSORPTION ON CHARCOAL, NUMBER 276-A, AT 100 TO 120°F.

Total Pressure At Equilibrium ATM	Volume Adsorbed, Liters (100°F, 1 ATM) / 100 GM. Charcoal	Composition of Adsorbed Phase, Mol. %. Hydrogen	Methane
	Feed, Mol. %: H_2 45%, CH_4 55%		
1	0.88	1.(0)	99.(0)
3	2.5	1.(5)	98.(5)
5	3.8	1.(7)	98.(3)
10	6.5	2.(6)	97.(4)
20	9.9	3.(2)	96.(8)
30	12.5	3.(2)	96.(8)
	Feed: H_2 63%, CH_4 37%		
1	0.90	0.(7)	99.(3)
5	3.7	1.(9)	98.(1)
10	6.6	2.(5)	97.(5)
	Feed: H_2 86%, CH_4 14%		
3	2.6	2.(1)	97.(9)
5	3.9	2.(2)	97.(8)
10	6.7	3.(0)	97.(0)
20	10.1	3.(1)	96.(9)
30	12.6	3.(3)	96.(7)

Heat of adsorption, K_g cal/gm mole, CH_4 = 4,500; C_2H_6 = 7,000.
Heat capacity of charcoal, c_p = 0.2.

TABLE 6

UTILITY AND EQUIPMENT COSTS

UTILITIES:	
Fuel Gas	20 ¢/million BTU (net)
Cooling Water, 85°F.,	2.0 ¢/1,000 Gal.
Steam, 150 lb./sq. in. abs.,	30 ¢/1,000 Lb.
Electric Power,	1.3 ¢/KWH
Air, 90°F, 5 lb./sq. in. gage,	2.1 ¢/1,000 cu. ft.
Flue Gas, 600°F, 5 lb. in. gage,	3.5 ¢/1,000 cu. ft.
PROCESS MATERIALS:	
Activated Charcoal, No. 276-A,	75 ¢/Lb.
Absorption Oil,	6.5 ¢/Gal.
DIFFUSION CELLS:	$1/Sq. Ft. Membrane Area.
COMPRESSORS, INCLUDING GAS ENGINE DRIVERS:	
1,000 HP and up, ΔP = 15 PSI,	$50/B.H.P.
1,000 HP and up, ΔP = 300 PSI,	$60/B.H.P.

TABLE 6
(Continued)

COLUMNS, CHARCOAL TOWERS, FLASH CHAMBERS

Working Pressure, Lb. per Sq. In. Gage	Diameter, Feet 3	6	9	12
	Dollars Per Foot-Length*			
0 - 100	$ 70	$132	$200	$310
100 - 300	100	220	400	650
300 - 500	132	268	580	1,020
Cost per Bubble-cap Plate, $	70	170	370	700
Cost per Column for Skirt or Support, $	250	600	1,000	1,500

* For top and bottom heads, add equivalent cost of ten feet additional length per vessel.

HEAT EXCHANGERS, SHELL AND TUBE TYPE DOLLARS PER SQ. FT. OF TUBE SURFACE

Pressure Lb. per Sq. In. Gage	Square Feet 100	200	300	500	1,000
50	$11.60	$6.50	$5.20	$3.95	$2.90
150	12.50	7.00	5.60	4.25	3.10
300	14.40	8.05	6.45	4.90	3.55
500	17.50	9.80	7.85	5.95	4.35

CENTRIFUGAL PUMPS WITH EXPLOSION PROOF MOTORS

COST IN DOLLARS

Head Lb. per Sq. In.	Gallons Per Minute Discharged 10	50	100	500	1,000	1,500
50	$ 700	$ 800	$ 900	$1,100	$1,300	$2,000
100	800	900	1,100	1,800	2,000	4,000
200	900	1,000	1,200	2,600	3,500	5,000
400	1,400	1,500	2,300	4,000	4,500	7,500

PRESSURE STORAGE VESSELS, ACCUMULATORS, ETC.

COST IN DOLLARS

Pressure Lb. per Sq. In. Gage	Capacity, Cu. Ft. 250	10,000	Over 10,000
15	$1,700	$ 6,000	
50	1,800	8,000	Use Multiples of 10,000 Capacity Vessels
100	1,900	10,000	
200	2,300	18,000	
400	3,200	34,000	

GAS HOLDERS, FOR 5 LB. PER SQ. IN. GAGE

Cu.Ft. Capacity	Cost In Dollars
50,000	25,000
100,000	45,000
150,000	62,000

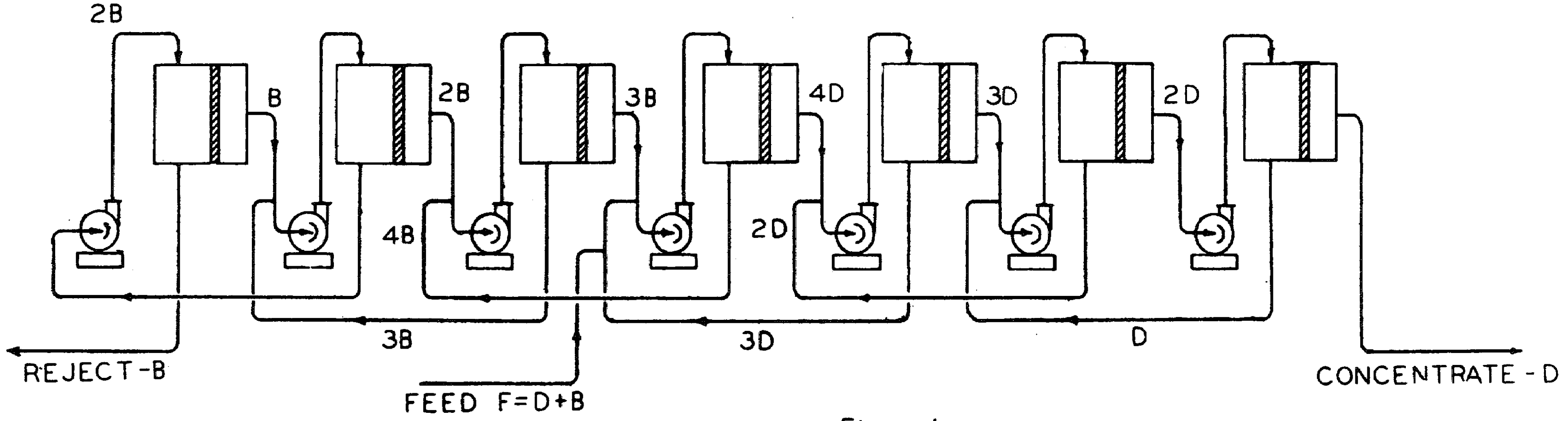

Figure I

Diffusion Stage Cascade

(F, D and B Refer to Volume Flow/Unit Time)