

Refinery Hydrogen Management: Cost Analysis of Chemically-Integrated Facilities

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Market forces and environmental legislation are increasing demand for hydrogen in oil refineries, while simultaneously restricting traditional hydrogen sources such as catalytic reforming. Effective recovery and efficient use of hydrogen are necessary if refiners are to maintain feedstock and product flexibility while avoiding unnecessary capital expenditure. A methodology for assessment of hydrogen resources is developed by analogy with the problem of process heat recovery. The effectiveness of hydrogen use is related to the cost of hydrogen recovery and the value added in hydrogen-consuming processes. The costs of hydrogen recovery by pressure-swing adsorption and membrane permeation are described. The value added in hydrogen-consuming processes and the availability of hydrogen are determined by the process chemistry and the prevailing economic conditions. A graphical display of the availability and distribution of hydrogen resources provides insight into refinery design and operations that supplements the information available from optimization by linear programming.

Introduction

Several current trends are causing demand for hydrogen in oil refineries to increase. Environmental legislation is increasing demand for hydrotreating, while reducing hydrogen production from catalytic reforming. The declining value of heavy fuel oil and shift to heavier crude oils also create increased demand for hydrogen. Since 1991, the U.S. oil industry has increased its hydrogen production and recovery capacity from 3.156 Gmol/day (2499 MMscf/day) to 3.703 Gmol/day (2932 MMscf/day) (Thrash, 1991; Williamson, 1994), with a further 0.648 Gmol/day (513 MMscf/day) planned or under construction (Riddle, 1994). This represents an increase of roughly 40% over 3 years. It is likely that not all of the additional hydrogen production capacity is necessary. The hydrogen produced in catalytic reforming, together with that which can be recovered from cracker and hydrotreater off-gases, is usually sufficient for the refinery's needs. In the past, therefore, there has not been a strong incentive to plan or coordinate hydrogen use across a site. As the demand for hydrogen increases and the supply is reduced, it is clear that the recovery of marginal hydrogen resources becomes worthy of consideration if unnecessary capital expenditure is to be avoided.

A refinery can be thought of as a set of processes that separate crude oil into fractions of varying hydrogen content and then attempt to move hydrogen from the lighter fractions to the heavier fractions to maximize the yield of high-value, midrange products. This simplified model ignores some processes that produce high-value products, for example, alkylation plants, lube oil plants, *etc.*; however, these plants have low flowrates, produce very valuable products, and do not affect the economics of the main fuel-producing processes. The refinery therefore contains some processes that are hydrogen sources and others that are hydrogen sinks. If we can recover more hydrogen from within the site, we reduce the amount of hydrogen that is sent to the furnaces with the off-gas, and we also reduce the need for hydrogen production. This can lead to significant savings in the cost of a new hydrogen production plant.

This problem is analogous to that of process heat

integration, in which we seek to minimize the utility requirements of a process by maximizing heat exchange between process streams. By exploiting this analogy, we develop a methodology for examining the availability and cost of hydrogen resources in the refinery. The deployment of these resources to maximize the value added can be addressed. The new methodology facilitates parametric and operational sensitivity analyses, allowing consideration of a range of operational and market scenarios. The information provided is supplementary to that obtained from optimization of refinery operations using linear programming (LP) and is presented graphically, giving the engineer visual insight into what is actually a rather nonlinear problem. Most importantly, the new methodology directly relates the overall performance of the refinery to the fundamental chemistry and economics of its constituent processes.

Background

The proposed techniques for integration of hydrogen resources are based on an analogy with process heat recovery. We can only recover heat from a heat source for use in a heat sink if the temperature of the source is greater than that of the sink. If we consider two process streams, we can plot the streams on a temperature–enthalpy diagram and the degree to which the lines representing the streams overlap will represent the scope for heat recovery (Figure 1). In reality, there must always be a minimum temperature approach (ΔT_{\min}) between the streams to provide a finite driving force for heat transfer. Real processes contain many streams, and we can lump the heat loads of the hot streams in each temperature interval to form a process “composite curve” that represents the total process heat source (Huang and Elshout, 1976). We can do the same thing for the process cold streams, and hence by examination of the overlap between the two composite curves we can set targets for external heating (Figure 2). The degree of overlap is determined by ΔT_{\min} , which imposes a heat-recovery pinch on the problem (Umeda *et al.*, 1978; Linnhoff *et al.*, 1979). A variety of techniques for analysis of heat recovery have been developed from this concept, of which reviews are given by Gundersen and Naess (1988) and Linnhoff (1993).

A closely related concept to the heat-recovery pinch is the “plus/minus principle”, which was formalized by

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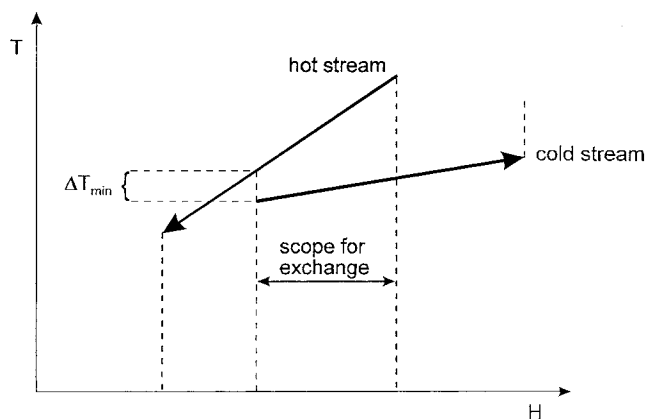


Figure 1. Temperature-enthalpy diagram for two streams exchanging heat.

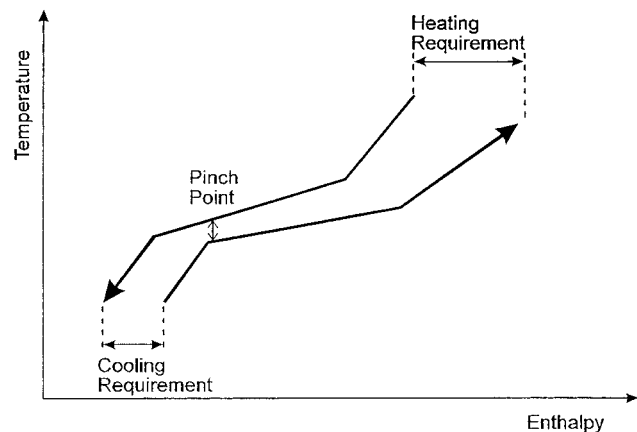


Figure 2. Composite heat curves for process heat recovery (Huang and Elshout, 1976).

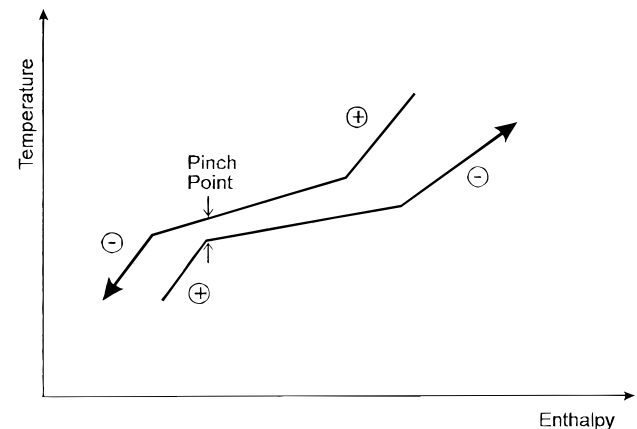


Figure 3. The "plus-minus" principle (Linnhoff and Parker, 1984).

Linnhoff and Parker (1984), although the principle was originally introduced by Umeda *et al.* (1979 a,b). This principle suggests that process modifications should be made that increase heat sources above the pinch and decrease heat sinks below the pinch (and vice versa for heat sinks, Figure 3). Once the process pinch temperature is located, this concept can be used to guide the generation of modifications that will lead to a net benefit in energy savings. It should be noted, however, that such modifications bring the curves closer together and hence reduce the available temperature driving force for heat transfer. The savings in energy will thus be offset by increased capital outlay, and a trade-off is necessary in design.

The concept of a recovery pinch has been extended to mass transfer (El-Halwagi and Manousiouthakis, 1989).

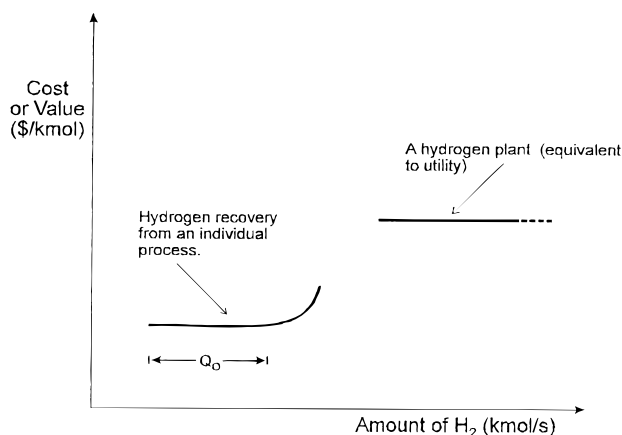


Figure 4. Typical refinery hydrogen sources.

In this case, the temperature-enthalpy diagram is replaced by a concentration-mass-load diagram. The results of such an analysis are useful in the design of mass-exchange networks for solvent-based systems, waste-water minimization, *etc.* It is clear that the pinch concept can be generalized to any transfer problem in which a driving force (*e.g.*, temperature or concentration) causes loads (*e.g.*, heat or mass) to be transferred from a set of process sources to a set of sinks.

The distribution of hydrogen resources in a refinery is similar to the pinch problems described above, in that we have a number of potential sources, each capable of producing a different amount of hydrogen, and a number of hydrogen sinks, each with different requirements. Where the problem is different is that we have considerable flexibility in deciding the hydrogen loads of individual units, since we are able to vary the throughputs of most units and can operate many of the processes over a wide range of conditions. As a result of this flexibility, we have considerable scope for optimization of refinery performance. We will discuss the relationship between our method for hydrogen management and overall refinery optimization later.

Theory

If we seek to analyze the distribution of hydrogen resources using techniques similar to pinch analysis, we must identify the driving force that causes transfer of hydrogen loads from source processes to sink processes. In a heat-exchanger network, a necessary condition to match two streams is that the hot stream has a greater temperature than the cold stream; however, a gas containing hydrogen can always be purified to deliver hydrogen that may then be used in any unit that consumes hydrogen. The only case in which we would choose not to purify a gas is when the cost is too expensive. Our driving force for recovery of hydrogen is therefore set by economics. Similarly, in our sink processes, we consume hydrogen to add value to our feedstock; therefore, the difference between the recovery cost and the value added represents the driving force for hydrogen transfer. We should only recover hydrogen when there is a financial incentive to do so; *i.e.*, when the net value generated in the sink process is sufficient to cover all of the costs of hydrogen recovery.

For any process that is a source of hydrogen we can plot the marginal cost of recovering hydrogen against the amount recovered (Figure 4). As we attempt to recover more hydrogen, the cost per kmol s^{-1} (or scf/day) increases, as shown in the curve on the left in Figure 4. Costs of hydrogen-recovery processes will be discussed in more detail later.

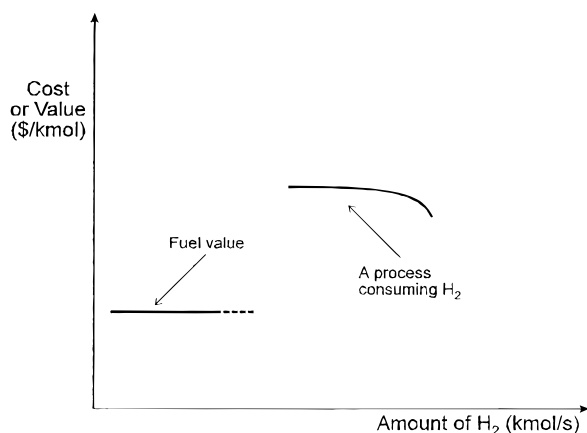


Figure 5. Typical refinery hydrogen sinks.

When the refinery has a hydrogen plant, it can be thought of as an external utility, the size of which is to be fixed in the design problem. The cost of hydrogen from the hydrogen plant is mainly a function of the feedstock price and does not depend strongly on the size of the hydrogen plant. In some cases, hydrogen is even purchased "over the fence", in which case a fixed price applies regardless of the amount purchased (*e.g.*, Patel *et al.*, 1994). We would usually not wish to recover hydrogen that was more expensive than that produced by the hydrogen plant; therefore, any portion of the source curve with a higher cost than the hydrogen plant represents an amount of hydrogen that is not economically recoverable and should be sent to site fuel.

For the processes that consume hydrogen we can similarly plot the value added per hydrogen consumed against the amount of hydrogen used (Figure 5). The value added per unit hydrogen consumed in each individual process is the value of the products of the process minus the cost of the feed (not including hydrogen) and any capital charge and other operating costs, all divided by the hydrogen consumption rate (eq 1).

$$VA_H Q = \sum_i w_i p_i - \sum_j v_j f_j - \sum_k C_{o,k} - C_C \quad (1)$$

where VA_H = value added per unit hydrogen consumed (\$/kmol or \$/Mscf), Q = flowrate of hydrogen (kmol/day or Mscf/day), p_i = flowrate of product i produced in the unit (m^3 /day or bbl/day), w_i = price of product i (\$/ m^3 or \$/bbl), f_j = flowrate of feed j consumed in the unit (m^3 /day or bbl/day), v_j = cost of feed j (\$/ m^3 or \$/bbl), $C_{o,k}$ = operating cost of utility k consumed in the unit (\$/day), and C_C = capital charge (\$/day). The cost of the feed consists of two components:

$$v_j = w_c + u_j \quad (2)$$

where w_c = price of crude oil (\$/ m^3 or \$/bbl), and u_j = processing cost incurred in upstream units (\$/ m^3 or \$/bbl).

The processing cost, u_j , is an appropriate charge to incorporate the costs of upstream units. For the purposes of this study, the costs of crude distillation and desalting can be shared between the fractions on a volumetric basis. The costs of the vacuum distillation can likewise be shared between the vacuum gas oil and the residue. It may reasonably be argued that this is an inappropriate basis and that the lighter fractions should bear a higher proportion of the costs. This is an important issue and should be given careful consideration when the method is applied industrially; however,

the equal assignment of costs is adequate here. Where the products of a process are themselves intermediates rather than finished products, *e.g.*, in heavy naphtha hydrotreating prior to catalytic reforming, the product value is found by allowing for the costs of downstream units in a suitable manner. For example, for the naphtha hydrotreater, the product value is taken as the value of gasoline minus the costs of the catalytic reformer. The effect of using alternative methods for valuing intermediate streams will be discussed below.

The product flowrates for the refinery processes, p_i , can be found in a number of ways. Maples (1993) and Gary and Handwerk (1994) published correlation charts relating product yields to feed properties such as API gravity, boiling range (or characterization factor), sulfur content, *etc.* and to process parameters such as degree of conversion, hydrogen use, *etc.* Such correlations can be coded into a spreadsheet or other software (Maples, 1995). Similar correlations are available in most operating and construction companies, or can be inferred from operating data. From these correlations we can predict the product yields at different levels of hydrogen consumption for hydrocrackers and the hydrogen rate required to achieve the product composition specifications in hydrotreaters. In principle, yield correlations could be replaced with a reliable chemical model of each refinery process, based, for example, on semiempirical quantum chemical calculations. Although there has been considerable research progress in this area recently (Broadbelt *et al.*, 1994; Neurock *et al.*, 1994), the computational effort required might not be justified in this application. Operating costs, $C_{o,k}$ are also correlated in Gary and Handwerk (1994) and Maples (1993).

The value added per unit hydrogen can be thought of as the total operating profit of the process, allowing for capital charges but not including hydrogen cost, on a basis of unit hydrogen consumption. If the cost of hydrogen fed to the process is less than this value added, then the process will be able to generate additional profit above that already stipulated in the capital charge factor. Where the capital cost of the process has already been written off then no capital charge need be applied.

For a typical process we require a certain minimum amount of hydrogen use, and the value added per unit hydrogen decreases at higher levels of use (for example, in hydrotreating there is no further return on reducing sulfur levels below the required limits).

We can combine the cost curves for all the sources of hydrogen in the refinery by adding the amounts of hydrogen available in each cost interval, in a manner analogous to the formation of composite heat curves. This gives us a composite source curve. Similarly, combining the sink curves gives a composite sink curve, which can be plotted on the same graph. The development of composite curves for a simplified refinery flowsheet is illustrated in the case study that follows.

Case Study 1

1. Design Basis. A study was carried out for the simplified refinery flowsheet shown in Figure 6. This case study was scaled from the case study presented in Gary and Handwerk (1994). The refinery was assumed to consist of crude and vacuum distillation units, naphtha, kerosene, and diesel hydrotreaters, a reformer, a catalytic cracker, a hydrocracker, and a coker. The refinery size was set at $1655 m^3/h$, *i.e.*, 250 000 barrels per standard day (bpsd) in the conventional units. This configuration would be typical for a world-scale refinery

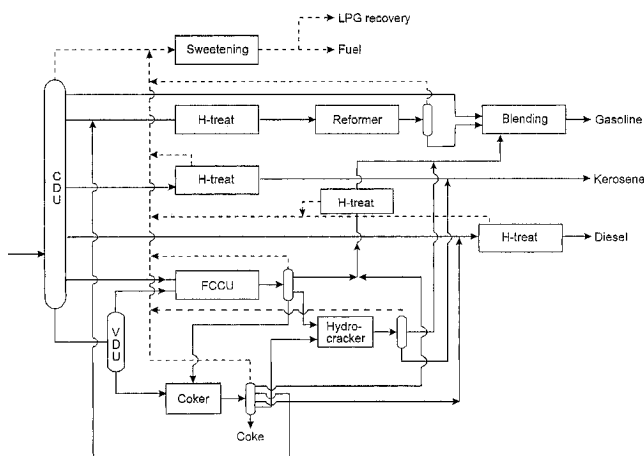


Figure 6. Simplified refinery flowsheet.

Table 1. Flowrates and Processing Destinations of Fractions Distilled from the Crude Oil in the Model Refinery

fraction	flowrate m ³ /h (bpsd)		processing destination
	ANS	Brent	
LSR gasoline	70.8 (10 700)	203.6 (30 750)	light gasoline blending
heavy naphtha	193.4 (29 213)	276.4 (41 750)	catalytic reformer
kerosene	172.6 (26 080)	208.5 (31 500)	hydrotreating for kerosene
light gas oil	301.2 (45 500)	302.9 (45 750)	hydrotreating for No. 2 diesel oil
heavy gas oil	339.3 (51 250)	62.9 (9 500)	catalytic cracking
vacuum gas oil oil	258.9 (39 110)	342.6 (51 750)	catalytic cracking

Table 2. Prices Used for Feeds and Products in the Refinery Case Studies^a

product	August 15, 1994 prices	price set 2
Alaskan North Slope crude oil	75.54 \$/m ³ (\$ 12.01/bbl)	81.77 \$/m ³ (\$ 13.0/bbl)
gasoline	151.39 \$/m ³ (\$ 24.07/bbl)	100.51 \$/m ³ (\$ 15.98/bbl)
heating oil (No. 2)	139.07 \$/m ³ (\$ 22.11/bbl)	121.65 \$/m ³ (\$ 19.34/bbl)
kerosene	139.07 \$/m ³ (\$ 22.11/bbl)	106.99 \$/m ³ (\$ 17.01/bbl)
isobutane	98.43 \$/m ³ (\$ 15.65/bbl)	76.61 \$/m ³ (\$ 12.18/bbl)
normal butane	91.14 \$/m ³ (\$ 14.49/bbl)	83.91 \$/m ³ (\$ 13.34/bbl)

^a Bell (1994).

on the West coast of the U.S.A. No attempt was made to optimize the flowrates of products from the crude unit, which were set at the values given by Gary and Handwerk (1994) and shown under "ANS" in Table 1. In practice, there would be some flexibility in adjusting the flowrates of different fractions to produce an optimal spectrum of refinery products. This does not affect our analysis, as we are only evaluating the curves for a single set of conditions. The processing destination of each fraction is also shown in Table 1. Alaskan North Slope crude oil (25.7°API, 0.99 wt % sulfur) was chosen, and prices for feeds and products were taken as the spot market values reported in the *Oil Gas J.* of August 15 1994 (Bell, 1994), summarized in Table 2. Process heat was costed at 2 \$/GJ, to allow for the cost of compressing air for the furnaces and boilers, cooling water was priced at 10¢ per thousand gallons circulated, and compressor work was costed at 3 ¢/kW h.

2. Process and Cost Models. Hydrogen Recovery Processes. Hydrogen is usually recovered from refinery off-gases using either membrane diffusion or pressure-swing adsorption (PSA). The key features of these processes are described by Abrardo and Khurana (1995). No published cost correlation was found for

either process, so it was necessary to develop correlations from the fundamental design equations, using cost and performance data available in the literature (Vervalin, 1994; Ratan, 1994; Ruthven *et al.*, 1994).

The cost of recovered hydrogen, C_H , is given by

$$C_H = C_F + C_W + C_R \quad (3)$$

where C_F = fuel value of recovered hydrogen (\$/kmol or \$/Mscf), C_W = cost of compressor work per unit hydrogen recovered (\$/kmol or \$/Mscf), and C_R = cost of the recovery process (\$/kmol or \$/Mscf).

The fuel value of the hydrogen is the cost of providing extra fuel to compensate for the calorific value of the hydrogen that was removed from the off-gas. This depends on the site fuel balance and varies from zero when the site has a net fuel surplus to the cost of an equivalent amount of natural gas when the site has a net fuel deficit. For the case study, C_F was taken as 0.396 \$/kmol (0.5 \$/Mscf).

The compressor work includes both feed and product compression. For PSA plants, only the product needs to be compressed if the inlet pressure is greater than 800 kN m⁻², while for membrane plants it may be necessary to compress both. For purposes of comparison, all hydrogen-recovery processes are costed to deliver hydrogen at the same pressure (2.86 MN m⁻² (400 psig) in this case). Where the product hydrogen is available at a higher pressure, a compressor work credit is applied. Compressor work, W_C , is calculated from

$$W_C = \frac{c_p T_1}{\eta} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (4)$$

where c_p = gas molar average heat capacity (J mol⁻¹ K⁻¹), T_1 = gas inlet temperature (K), P_1 = inlet pressure (N m⁻²), P_2 = delivery pressure (N m⁻²), γ = ratio of gas specific heats, and η = isentropic efficiency of compression, typically 0.85. For refinery gases it is adequate to assume $\gamma = 1.4$; however, care must be taken in evaluating c_p , as this is quite sensitive to the composition and compression ratio.

For PSA processes, the cost of the recovery process can be estimated from eq 5, which is derived in Appendix A:

$$C_R (\$/1994/\text{kmol}) = \frac{18.04}{Q} + \frac{0.2364}{Yz} \quad (5)$$

where Y = recovery yield of hydrogen, z = feed gas hydrogen mole fraction, and Q = production rate of purified hydrogen (kmol/h). In typical refinery applications, the cost of PSA processes is almost independent of the purity of hydrogen produced (Miller and Stoecker, 1989).

For the membrane process, the area required, A , is given by Hogsett and Mazur (1983) as

$$A = \frac{YGz}{R_p P_L \left[r \left(\frac{z - x_r}{\ln \left(\frac{z}{x_r} \right)} \right) - y \right]} \quad (6)$$

where G = gas feed rate (kmol/h or MMscf/day), R_p = membrane permeability (kmol N⁻¹ h⁻¹ or MMscf/(ft² psi day)), P_L = delivery pressure (N m⁻² or psi), r = pressure ratio, y = hydrogen purity, and x_r = hydrogen

concentration in the residual gas, given by

$$x_r = \frac{y(1 - Y)z}{(y - Yz)} \quad (7)$$

From eq 6 we can form a group:

$$\frac{AR_p P_L}{YzG} = \frac{AR_p P_L}{Q} = \frac{1}{\left[r \left(\frac{z - x_r}{\ln \left(\frac{z}{x_r} \right)} \right) - y \right]} \quad (8)$$

We then find eq 9, which is derived in Appendix A, where a version in conventional refinery units is also given.

$$C_R (\$/1994/\text{kmol}) = 0.0391 + 0.0114 \frac{AR_p P_L}{Q} \quad (9)$$

Care must be taken in applying either of these correlations, and neither should be used to extrapolate beyond the range of the data on which they are based. Again, the cost is not strongly dependant on purity in the range of interest, so for convenience we set the purity of recovered hydrogen at 99%, which is adequate for most refinery purposes. Some advantages can be obtained from using purer hydrogen in certain refinery processes. This will be discussed later.

We can use the equations above to find the cost of recovering hydrogen from any off-gas at different values of the recovery yield, Y . Since the recovered hydrogen is essentially pure, we can write the amount of hydrogen recovered as:

$$Q = GYZ \quad (10)$$

The total cost C_T (\$) is then

$$C_T = QC_H \quad (11)$$

and the marginal cost C_M (\$/kmol or \$/Mscf) is

$$C_M = \frac{\delta C_T}{\delta Q} \quad (12)$$

where δC_T is the extra total cost incurred in increasing the yield Y to give extra marginal production δQ .

The condition

$$C_M = C_H \quad (13)$$

determines the base-case recovery Y_0 and production Q_0 . Increasing the recovery beyond this allows extra production, but at increasing marginal cost. When we plot the marginal production versus the marginal cost we obtain a curve of the type shown in Figure 4. Figure 7 shows the marginal cost of recovering hydrogen from the reformer off-gas using both processes for our example. For the membrane process, the relationship between amount recovered and marginal cost is highly nonlinear at high recoveries. For the PSA process, the recovery cost is directly proportional to the throughput (see Appendix A) and hence the marginal cost profile is a straight line. In the design problem we would cost both recovery processes and then select the cheapest. Occasionally, the PSA process will be cheapest, but the membrane process will permit a higher recovery, albeit at lower purity. In such cases the choice of recovery process is not straightforward, as the value of the additional hydrogen recovery obtainable by using the

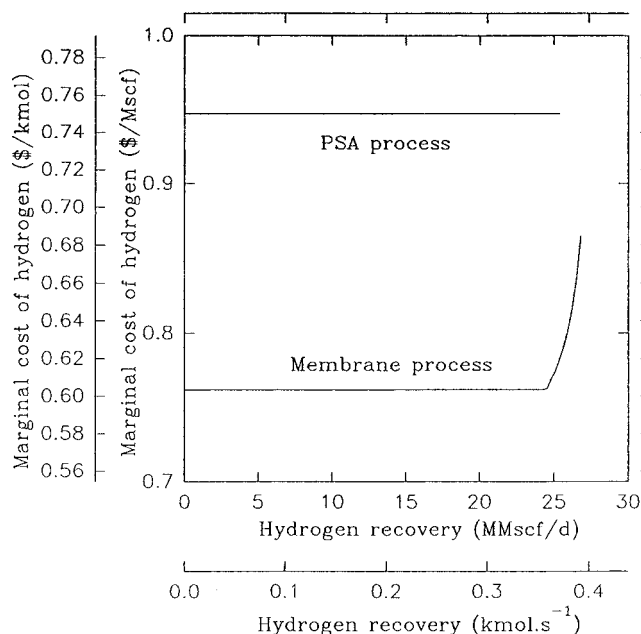


Figure 7. The cost of recovering hydrogen from the reformer off-gas.

membrane process depends upon the overall hydrogen balance of the refinery. We will return to this issue later. If some of the off-gases contain hydrogen at high pressure and high purity then it may be possible to use these gases directly without purification. This should be considered when designing the hydrogen distribution system; however, by including recovery costs at this stage we make a safe-side approximation. If the refinery already has a hydrogen recovery plant then the appropriate cost curve is used for the process that is in operation. For the case study, the membrane process was chosen in all cases, as this maximizes the overall recovery of hydrogen. The feed conditions for all of the hydrogen source gases are summarized in Table 3.

Refinery Processes. The major process units were scaled directly from the results given in Gary and Handwerk (1994), with the exception of the hydrocracker, which was evaluated at a range of different hydrogen consumption rates. A high consumption of hydrogen (4.77 kmol/m³ or 600 scf/bbl) was chosen for the diesel hydrotreater, corresponding to production of low-sulfur diesel oil (0.05 wt %) (Nutmagul, 1995). Details of other design assumptions are given in Serriere (1994). Operating costs for the processes were similarly estimated from Gary and Handwerk (1994) and Vervalin (1994). Such cost predictions are necessarily inaccurate; however, they are adequate for the purposes of illustrating the method. It was assumed that all capital costs for the main refinery units had been amortized. The value added in the kerosene hydrotreater is calculated as an example in Appendix B.

3. Generation of the Cost and Value Composite Curves. Once we have obtained the cost and yield data it is relatively simple to plot how the cost or value added varies with the amount of hydrogen produced or consumed. For example, Figure 7 shows the marginal cost of recovering hydrogen from the reformer off-gas against the amount of hydrogen recovered for both processes. In this case, the membrane process is selected as the cheapest. We can plot similar curves for all of the hydrogen source processes on the same graph (Figure 8). We can then add the marginal amounts of hydrogen available in each marginal cost interval to give the

Table 3. Feed Conditions for the Hydrogen Source Gases

hydrogen-containing source gas	feed gas flow (mol/s)			pressure (MN m ⁻²)	hydrogen mole fraction
	case 1	case 2	case 3		
reformer off-gas	485.4	485.4	607.6	1.21	0.85
hydrocracker high-pressure purge	20.8	20.8	12.9	12.51	0.75
hydrocracker low-pressure purge	93.1	93.1	57.9	1.96	0.5
heavy naphtha hydrotreater purge	11.8	11.8	14.8	2.86	0.9
cracked naphtha hydrotreater purge	108.5	63.2	69.5	2.86	0.9
kerosene hydrotreater purge	67.8	67.8	81.9	7.00	0.9
diesel hydrotreater purge	318.7	214.0	271.7	7.00	0.9

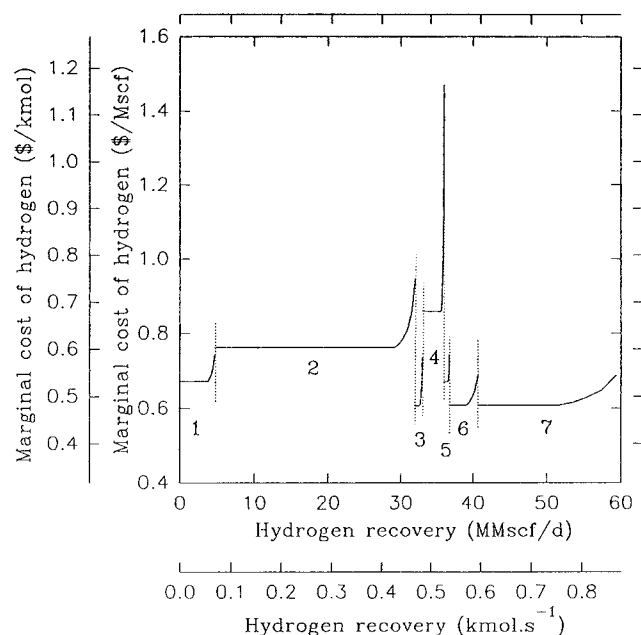


Figure 8. The costs and recoverable amounts of hydrogen from all of the hydrogen source processes. Legend: 1, cracked naphtha hydrotreater purge; 2, reformer off-gas; 3, hydrocracker high-pressure purge; 4, hydrocracker low-pressure purge; 5, heavy naphtha hydrotreater purge; 6, kerosene hydrotreater purge; 7, diesel hydrotreater purge.

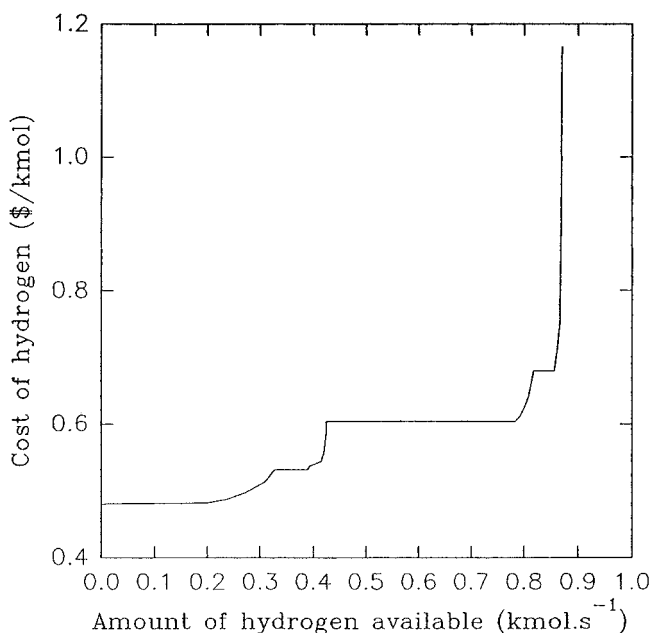


Figure 9. The composite cost curve for the hydrogen source processes.

source composite curve (Figure 9). This is easily performed on a spreadsheet or coded into software. The part of the source curve where the cost of hydrogen is less than the cost of hydrogen produced in the hydrogen plant ("utility hydrogen") represents the scope for

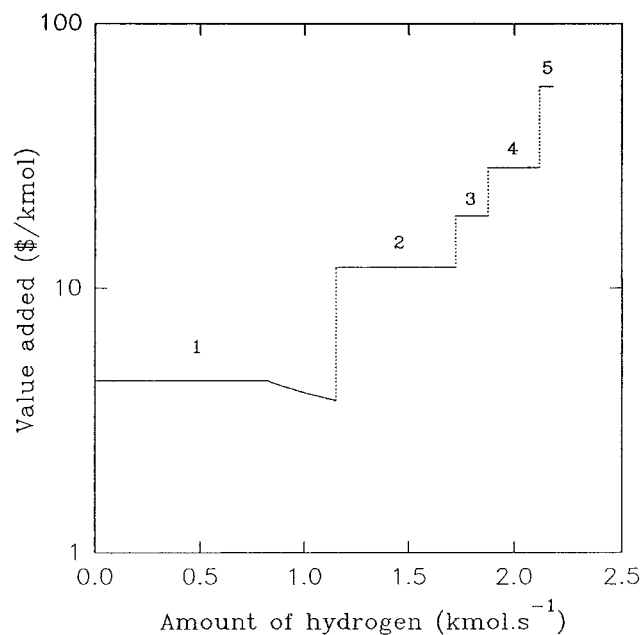


Figure 10. The composite cost curve for the hydrogen sink processes. Legend: 1, hydrocracker; 2, diesel hydrotreater; 3, kerosene hydrotreater; 4, cracked naphtha hydrotreater; 5, heavy naphtha hydrotreater.

hydrogen recovery in the refinery. This could be the entire region in some cases. The remainder of the hydrogen sink requirement will be met from the hydrogen plant, giving the target for hydrogen production. The cost of producing hydrogen from methane in a steam-reforming plant is estimated to be 1.62 \$/kmol (\$ 2.05 per Mscf) (updated from Baade *et al.*, 1993); therefore, the target for hydrogen recovery is that part of the source curve below this cost, *i.e.*, 0.860 kmol s⁻¹ (58.8 MMscf/day). Any marginal hydrogen source of cost greater than the cost of utility hydrogen represents an amount of hydrogen that is not economically recoverable and should be sent to site fuel. The costs of recovering hydrogen from the catalytic cracker off-gas and the coker off-gas could not be estimated reliably, as the feed concentrations of hydrogen in these gases are well outside the range of the cost correlations; however, Mitariten (1995) stated that hydrogen in these gases is not economically recoverable.

We can follow the same procedure to form a composite curve for the sink processes (Figure 10) and then plot the two composite curves on the same graph (Figure 11). For the hydrogen consumptions indicated in the sink processes, the total hydrogen demand is 2.180 kmol s⁻¹ (149.1 MMscf/day), hence the target for hydrogen plant production under these conditions is 1.320 kmol s⁻¹ (90.3 MMscf/day). Note that the value composite curves have been plotted on a logarithmic scale because of the high value added in the naphtha hydrotreaters. This is a result of the small amount of hydrogen used in this process and the method of assigning crude distillation costs.

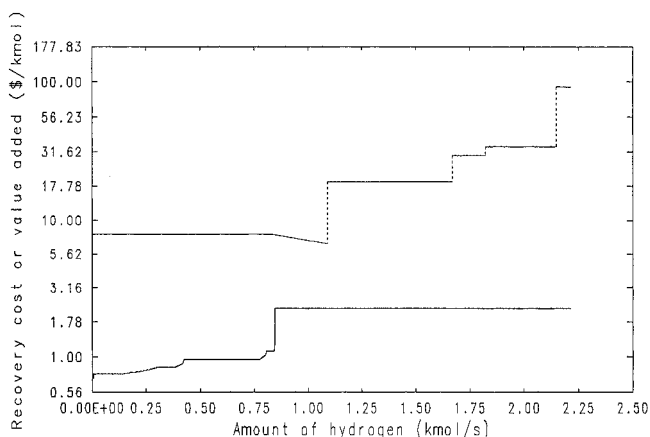


Figure 11. The value composite curves for the refinery of case study 1.

The sink curve lies above the source curve, as it always would, ideally, showing that under the conditions of our case study, all of the processes are making a satisfactory return on investment. This is not surprising, bearing in mind the low price of Alaskan North Slope crude oil. If the curves touch, we have a pinch point and the processes that form the composite at this point are delivering the minimum specified rate of return, assuming that capital costs are incorporated into the hydrogen costs via a capital charge factor. If a capital charge factor is not included then these processes are just breaking even. If there were any region where the curves crossed, then the sink processes concerned would not be giving the required return on investment. The analysis is perhaps more interesting when one or more processes are not delivering satisfactory performance. This will be discussed below. The diagram therefore gives a rapid overview of the refinery economic performance and shows the targets for hydrogen recovery, hydrogen plant output, and hydrogen contribution to site fuel.

It should be stressed that many of the assumptions made above are not necessary if the analysis is applied to a real refinery where operating data are available. In such a case, the study should be based on the existing data rather than on published correlations of product yields and costs. This has been attempted for a real refinery similar to the one described, giving broadly similar results (Thomas, 1994); however, the results are confidential.

Applications

The proposed method can be used in support of refinery operations, in design sensitivity analysis, and in testing alternative expansion plans. The design and operation of a refinery are not steady-state problems, and many of the costs associated with refinery operation can fluctuate widely on an almost daily basis. Both feed and product prices undergo large variations, and some refineries must also be able to process very different crude oils, with resulting changes in unit throughputs and product slate. Refinery operations can be optimized efficiently using linear programming (LP) methods based on the simplex algorithm (Dantzig, 1963). Although the actual behavior of the refinery processes may be significantly nonlinear, the problem has many linear constraints and over relatively narrow operational ranges it is acceptable to develop a computer model based on linear approximations of process behavior. Optimization algorithms not only determine the opti-

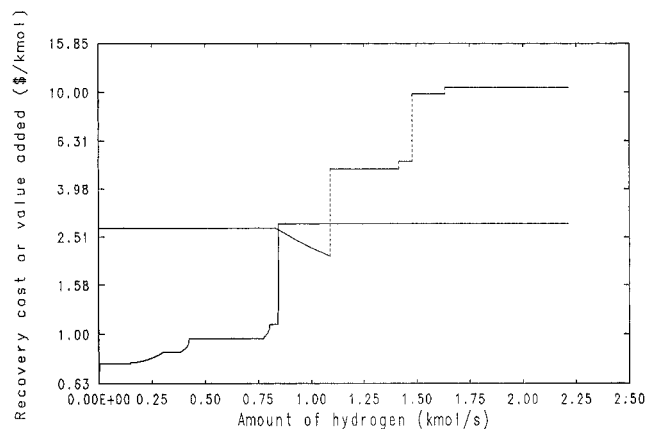


Figure 12. The value composite curves for case study 1, price set 2.

mum operating conditions but also provide sensitivity analysis in the form of "marginal prices" that indicate the effective value of changing the constraints on the problem. This is very useful information, since in a typical refinery LP optimization, with several hundred variables, all but a few will be set at upper or lower constraint limits.

The demand for hydrogen is an important variable in refinery optimization, as it sets the duty of the hydrogen plant, which is a process that consumes feedstock, but does not directly produce externally-marketable products. In a typical LP optimization model, each source of recovered hydrogen would be described by a linear or scalar cost function and a maximum recovery constraint. Figures 7 and 8 show that although such assumptions are reasonable for PSA processes, the actual variation of marginal cost is highly nonlinear at high recoveries when the membrane process is used; therefore, unless care is taken in formulating appropriate functions to describe this behavior in the LP model, the model will be inaccurate and sub-optimal performance will result. The value composite curves provide a visual representation of the nonlinear subproblem of hydrogen management that forms a part of the overall optimization. As such, they cannot be used to independently determine the optimal operation of the refinery; however, they can show how individual processes are performing and how that performance could be improved. This might suggest rearrangements of the hydrogen distribution scheme that would enable the LP optimizer to find more profitable ways of running the refinery. The curves therefore supplement the "marginal price" information available from the LP model and provide visual information that is easy to interpret.

For example, in the set of curves shown in Figure 12 there is a region where the curves overlap, *i.e.*, where the processes concerned are making a loss. These curves correspond to the same process flowrates as the previous example (Table 3), but with the fictitious set of prices given as "Price Set 2" in Table 2 and the price of process heat raised to \$ 3/GJ. We can generate strategies for enhancing profitability using the value equivalent of the "plus-minus" principle (Linnhoff and Parker, 1984) and rapidly evaluate them if we have a computer program to generate the curves. In this example, performance could be improved by reducing hydrocracker severity (1) or increasing reformer throughput (2) (*e.g.*, by blending in some lighter crude oil with the feed to the refinery). Either of these changes would reduce the area of overlap. Ideas for operational changes can then be evaluated using the LP optimiza-

tion model. The visual insight gained from the value composite curves thus complements the numerical power of the optimization model.

The value composite curves also throw some light on the design of hydrogen recovery processes and hydrogen-consuming processes. If we wish to choose between a PSA plant or a membrane plant that has slightly higher costs but higher recovery then we can examine the value composite curves for each case under a range of likely price scenarios and see which design is more likely to cause a value "pinch". If the hydrogen flowrate is large and the site has an overall hydrogen deficit, then the additional recovery in the membrane process may justify the extra cost. Similarly, we can use the curves to examine the effect of purity of recovered hydrogen. In general, the hydrogen-consuming processes are carried out in packed bed reactors at high temperature and pressure, with liquid feed and products and a gas recycle. Hydrogen is brought in as make-up gas, and a purge is taken to prevent buildup of light hydrocarbon gases in the recycle. A more pure hydrogen feed will reduce the amount of purge gas that must be drawn off and hence will also reduce the feed rate and feed compression work. The membrane process is, however, inherently unsuited to producing very high purity hydrogen (>99%), and the PSA process will have a lower recovery, particularly at high purity. The effect of increasing the purity of hydrogen in the feed to one process on all of the other refinery processes is easily investigated by plotting the curves for the alternative designs under a range of likely price scenarios. The curves can also be used to assess design alternatives that reduce hydrogen use by process rearrangements (Nutmagul, 1995) or by changing the hydrogen concentration in the recycle gas, and also potential changes that would increase hydrogen consumption, *e.g.*, reducing the product sulfur concentration. In some cases, it may be felt that some of the hydrogen sources are too small to warrant recovery. Again, the effect on overall refinery performance is easily examined by comparing the curves for alternative designs, in conjunction with the output of the LP optimizer.

A further application is in the testing of alternative expansion plans. If new capacity is to be added to any refinery unit, the effect on the operation of all other units under a wide range of conditions is easily examined. This may be of particular help in assessing the changeover to reformulated gasoline or to heavier crudestocks, as discussed in case studies 2 and 3 below. Potential areas that might suffer adverse economic consequences can be identified and the new units sized to make the best use of the capital expenditure under the most likely range of operating conditions. Such an analysis would be of value to a contracting company, which could thus demonstrate to a potential client that the design tendered was most appropriate to the client's needs. Different sites will have different sensitivities; therefore, when choosing between several refineries, the most attractive site for a potential modification can be identified.

Case Study 2

Changing Product Grade. The refinery presented in the base case was designed to produce low-sulfur diesel (0.05 wt % S) and gasoline (50 ppmw S). Suppose we initially had a refinery that was producing diesel at 0.5 wt % sulfur and gasoline at 100 ppmw sulfur, and we had to convert to lower-sulfur products, with no expectation of an increase in product prices. The gas flows for this case are given under "case 2" in Table 3, and the corresponding composite curves are shown in

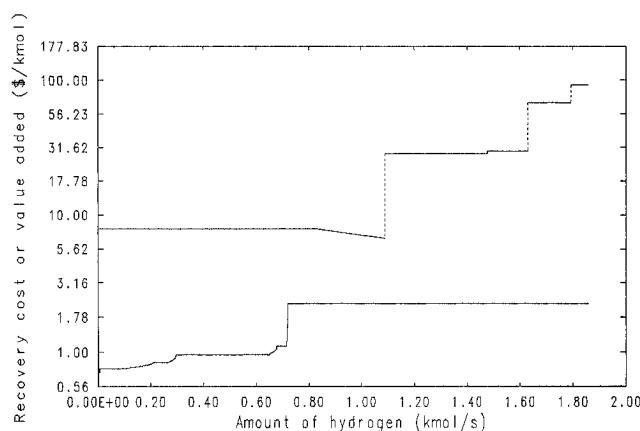


Figure 13. The value composite curves for case study 2.

Figure 13. Comparing Figure 11 with Figure 13, we see that there is a significant decrease in value added per unit hydrogen for both the diesel hydrotreater and the cracked naphtha hydrotreater when we switch to low-sulfur products. The total hydrogen demand increases from 1.86 to 2.21 kmol s⁻¹ (19%); however the potential for hydrogen recovery also increases, so that the target for hydrogen plant output increases by roughly the same ratio (1.14 to 1.37 kmol s⁻¹, *i.e.*, 20%). If the hydrogen plant could not supply this additional demand then the refiner would have four options: build additional hydrogen plant capacity; arrange an "across the fence" hydrogen supply; adapt refinery operations to reduce hydrogen demand; or blend in a light crude with the feed to reduce hydrogen demand and increase the supply of hydrogen from the reformer. Examination of the composite curves for the low-sulfur case (Figure 11) shows that the least difference between hydrogen cost and value added occurs in the hydrocracker; therefore, if hydrogen plant output is constrained we would expect to have to reduce the hydrocracker throughput. We also see that there is little advantage in purchasing outside hydrogen at a cost greater than 5 \$/kmol in order to maintain hydrocracker throughput. If we wish to maintain full utilization of our plant then the most attractive option is probably to blend in a lighter crude oil so as to increase hydrogen production and recovery. The value composite curves for a lighter crude oil are given in the example that follows.

Case Study 3

Converting from Light to Heavy Crude Oil. In this case study we examine how the value composite curves can be used in assessing the changeover from processing a light crude oil, such as Brent, to a heavy crude oil, such as Alaskan North Slope. The refinery configuration and the prices of all products remain the same, and we continue to produce low-sulfur diesel in both cases. In practice, the refinery would probably not have sufficient heavy-end capacity for such a radical change of feedstock if it had been designed to process a light, sweet feed; however, we will concern ourselves only with the effects on the hydrogen system and neglect capacity restrictions elsewhere in the refinery. The flowrates of the crude distillation products for this case are shown under "Brent" in Table 1. The Brent crude oil price was taken as 115.73 \$/m³ (18.4 \$/bbl). When Brent crude oil is run, we obtain the gas flows under "case 3" in Table 3. The value composite curves for this case are shown in Figure 14. The total recoverable hydrogen is slightly higher at 0.863 kmol s⁻¹ (59 MMscf/day), although a greater proportion of the hydrogen is available from the reformer at a higher cost than hydrogen recovered from the hydrotreaters. For Brent

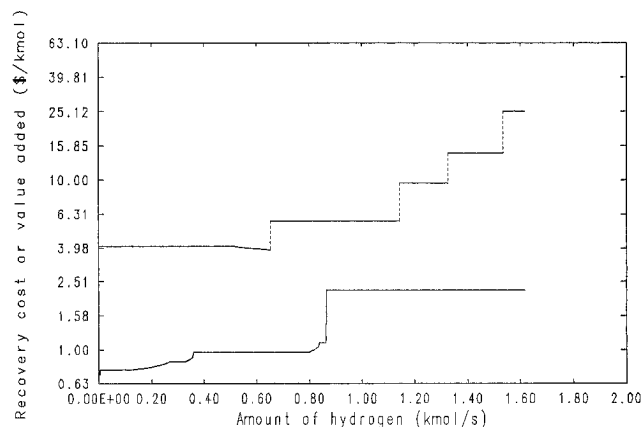


Figure 14. The value composite curves for case study 3.

crude oil, the hydrogen requirements for distillate hydrotreating are greater than for ANS because of the higher proportion of distillates in the crude oil. The amount of hydrogen required for hydrocracking is substantially reduced, however, leading to an overall hydrogen requirement of 1.62 kmol s^{-1} (110.5 MMscf/day), which could be satisfied with a hydrogen plant or off-site purchase of $0.750 \text{ kmol s}^{-1}$ (51.3 MMscf/day). If we wished to convert the refinery from running Brent crude oil (Figure 14) to running ANS crude oil (Figure 11) then we would face a deficit of 0.62 kmol s^{-1} (42.1 MMscf/day) of hydrogen production, which is enough to warrant construction of an additional hydrogen plant. The advantage of switching to a heavier crude oil would be a significant improvement in operating margins, particularly for diesel hydrotreating. We might also consider rearranging the hydrogen distribution system after the change of crude oils, to take advantage of the change in position of the sink curves relative to the source curve.

Discussion

As mentioned above, there is considerable scope for variation in the methods used to cost fractions, particularly for the intermediate fractions. This can have a marked effect on the results; however, it does not detract from the viability of the overall approach. Since the approach is most useful in sensitivity analysis and operations support, it does not really matter what basis is chosen as long as it is applied consistently. Careful consideration should be given to the choice of basis when applying the method industrially; however, there is no need to make an arbitrary assignment of costs where commercial data are available, as already mentioned.

It may be possible to apply this methodology to the analysis of other problems besides refinery hydrogen. The method of forming cost and value composites for assignment of resources of a chemical is entirely general and could be applied to any site or complex in which a common chemical species was produced and consumed in several different plants or facilities. Other examples (*e.g.*, chlorine and benzene) are the subject of continuing research. Further research is also needed to extend this methodology to the design of hydrogen distribution networks.

Conclusions

The method presented in this paper is a novel tool for the economic analysis of large integrated sites such as oil refineries. It gives the engineer a simple, graphical insight into refinery profitability that is based on an understanding of process design and operation fundamentals. The results are complementary to the predictions of LP optimization and can be generated

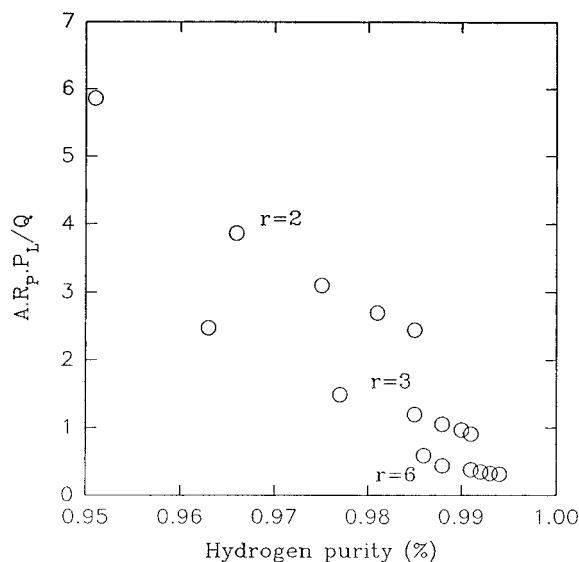


Figure 15. Correlation of membrane process performance data.

from simple equations that are easily coded into software. The tool allows rapid identification of the areas of a refinery that are underperforming economically and can be useful in suggesting and testing remedies. The method is also useful in design sensitivity analysis. Careful consideration must be given to the definition of the cost basis when applying the method in industrial practice.

Nomenclature

- A = membrane area (m^2 or ft^2)
- a, b, a', b' = fitting constants
- C_C = capital charge (\$/day)
- C_F = fuel value of recovered hydrogen (\$/kmol or \$/Mscf)
- C_H = cost of recovered hydrogen (\$/kmol or \$/Mscf)
- C_{MEM} = annualized capital cost of a membrane permeation plant (\$/yr)
- $C_{o,k}$ = operating cost of utility k consumed in a process unit (\$/day)
- C_{PSA} = annualized capital cost of a pressure-swing adsorption plant (\$/yr)
- C_R = cost of the recovery process (\$/kmol or \$/Mscf)
- C_T = total cost of hydrogen production (\$)
- C_W = cost of compressor work per unit hydrogen recovered (\$/kmol or \$/Mscf)
- c_p = gas molar average heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$)
- f_j = flowrate of feed j consumed in a process unit (m^3/day or bbl/day)
- G = gas feed rate (kmol/h or MMscf/day)
- N_y = operating hours per year (h/yr)
- P_1 = compressor inlet pressure (N m^{-2})
- P_2 = compressor delivery pressure (N m^{-2})
- P_L = delivery pressure for gas produced in a membrane separator (N m^{-2} or psi)
- p_i = flowrate of product i produced in a process unit (m^3/day or bbl/day)
- Q = flowrate of hydrogen (kmol/h or Mscf/day)
- Q' = flowrate of hydrogen (kmol/day or Mscf/day)
- Q_0 = base-case production of hydrogen (kmol/h or Mscf/day)
- R_p = membrane permeability ($\text{kmol N}^{-1} \text{h}^{-1}$ or $\text{MMscf}/(\text{ft}^2 \text{psi day})$)
- r = pressure ratio in the membrane process
- T_1 = compressor gas inlet temperature (K)
- u_j = processing cost incurred in upstream units (\$/ m^3 or \$/ bbl)
- VA_H = value added per unit hydrogen consumed (\$/kmol or \$/Mscf)
- v_j = cost of feed j (\$/ m^3 or \$/ bbl)

W_C = compressor work (W)
 w_c = price of crude oil (\$/m³ or \$/bbl)
 w_i = price of product i (\$/m³ or \$/bbl)
 x_r = hydrogen concentration in the residual gas from the membrane process
 Y = recovery yield of hydrogen
 Y_0 = base-case recovery
 y = hydrogen purity
 z = feed mole fraction of hydrogen
 ΔT_{\min} = minimum temperature approach
 γ = ratio of gas specific heats
 η = isentropic efficiency of compression

Abbreviations

CDU = crude oil distillation unit
 FCCU = fluid catalytic cracking unit
 LP = linear programming
 PSA = pressure-swing adsorption
 VDU = vacuum distillation unit

Appendix A

Costs of Hydrogen Recovery Processes. 1. Pressure-Swing Adsorption. Ruthven *et al.* (1994) provide an excellent description of the fundamentals, modeling and design of PSA processes. They do not give cost data; however, on pages 6 and 7 they state that the capital cost is a linear function of throughput, *i.e.*

$$C_{\text{PSA}} = a + bG \quad (14)$$

where C_{PSA} = capital cost of a PSA plant and a and b are fitting constants.

Wall (1982) provides cost data for three PSA units of different sizes performing the same duty, which, when plotted, confirms eq 14. The cost data given by Wall (1982) is outdated, and it is not appropriate to update the costs using standard plant cost indices, as PSA is a relatively new technology for which costs will not behave in the same manner as for standard process equipment. Vervalin (1994) provides more recent cost data, giving ranges of cost and ranges of operating conditions, from which the conditions of least and greatest throughput are easily determined. For the PSA process the major costs are capital cost and cost of compression (already accounted for in eq 3). We can therefore rearrange (14) to give the recovery per unit production:

$$C_R = \frac{C_{\text{PSA}}}{N_y Q} = \frac{a'}{Q} + \frac{b'G}{Q} \quad (15)$$

i.e.,

$$C_R = \frac{a'}{Q} + \frac{b'}{YZ} \quad (16)$$

Fitting the data of Vervalin (1994), we obtain

$$C_R = \frac{0.4330}{Q} + \frac{0.2986}{YZ} \quad (17)$$

where C_R is in \$₁₉₉₄/Mscf and Q is in MMscf/day, or

$$C_R (\text{\$/kmol}) = \frac{18.04}{Q} + \frac{0.2364}{YZ} \quad (18)$$

where C_R is in \$₁₉₉₄/kmol and Q is in kmol/h. This correlation is a crude approximation based only on the assumption of cost being proportional to throughput; therefore, it is not appropriate to specify a range for each of the design variables. In practice, however, hydrogen recovery using PSA is usually only attractive for feeds

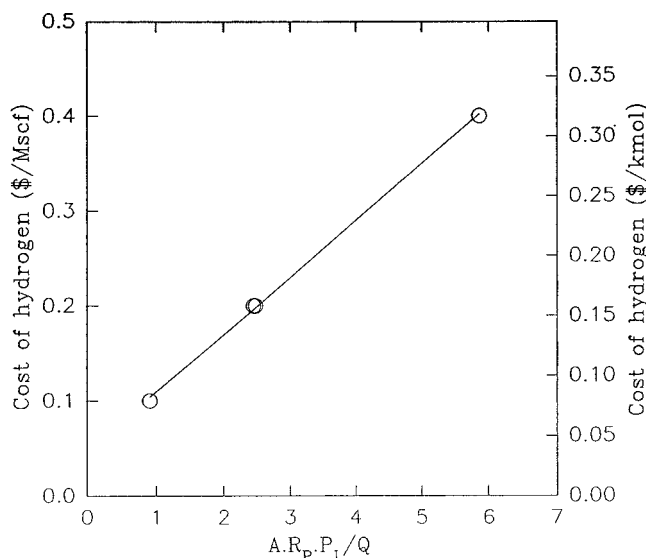


Figure 16. Correlation of membrane process capital cost per unit production.

containing more than 40 mol % hydrogen, and recovery yields are less than 90%.

2. Membrane Permeation. The recovery cost of membrane permeation units per unit production can be correlated with the dimensionless group $AR_p P_L/Q$, derived in the main text from the design equation given by Hogsett and Mazur (1983). Ratan (1994) provides an extensive set of typical operating data relating product purity to recovery yield at different pressure ratios. From this data we can calculate the values of the parameter $AR_p P_L/Q$, which are plotted in Figure 15.

Vervalin (1994) gives ranges of costs at different pressure ratios. If we plot the highest and lowest values of $AR_p P_L/Q$ against the highest and lowest costs for the same pressure ratio, we obtain a linear correlation (Figure 16). This is fitted by

$$C_R = 0.04935 + \frac{0.06015 AR_p P_L}{Q} \quad (19)$$

where C_R is in \$₁₉₉₄/Mscf and Q is in MMscf/day, or

$$C_R = 0.0391 + \frac{0.0114 AR_p P_L}{Q} \quad (20)$$

where C_R is in \$₁₉₉₄/kmol and Q is in kmol/h. This correlation should only be used in the range over which the data was fitted, *i.e.*, recovery yields from 0.4 to 0.95, pressure ratios from 2 to 6, and purities from 0.93 to 0.995. The parameters Y , y , and r are not independent, and in general a higher pressure ratio is required to increase the recovery of hydrogen at constant purity. Calculation of recovery–purity profiles is described in Ruthven *et al.* (1994). For the purposes of this study the commercial data reported by Ratan (1994) was correlated by the expression:

$$y = 0.995 - (0.0938 Y + 0.369 Y^{6.78}) r^{2.02} \quad (21)$$

which gives a good fit to the data and can be used for interpolation over the range indicated.

N. B.: C_R is the capital cost per unit product. The capital cost of the membrane unit C_{MEM} is given by

$$C_{\text{MEM}} = C_{\text{R}} Q = \left(0.04935 + \frac{0.06015}{r \left(\frac{z - x_{\text{T}}}{\ln \left(\frac{z}{x_{\text{T}}} \right)} \right) - y} \right) Q \quad (22)$$

i.e., the total capital cost is proportional to the flowrate, which is what we would expect for a membrane process.

Appendix B

Sample Calculation of Value Added. The following example illustrates how we calculate the value added in the kerosene hydrotreater. Conventional refinery units are used for ease of comparison with the source reference.

The feed is 26 080 bpsd of 38.9°API straight-run kerosene at price 12.187 \$/bbl, including the costs of upstream processing. From the feed properties we can estimate the hydrogen and utility consumption using schedule "B" of Table 9.1 on page 195 of Gary and Handwerk (1994). These are

hydrogen	400 scf/bbl (i.e., 10.43 MMscf/day or 0.152 kmol/s)
steam	8 lb/bbl
power	3.0 kW h/bbl
fuel	0.15 MMBtu/bbl
catalyst	0.03 \$/bbl

In addition, we must include the cost of compressing the feed hydrogen from our reference pressure of 2.86 MN m⁻² to the process pressure of 7.0 MN m⁻², which requires a further 0.45 kW h/bbl. The sum of utility costs is therefore 0.490 \$/bbl feed. The value of the product kerosene is 22.11 \$/bbl (Table 2). Substituting into eq 1:

$$\text{VA}_{\text{H}} \times 0.400 \times 26\,080 = (26\,080 \times 22.11) - (26\,080 \times 12.187) - (26\,080 \times 0.490) - 0$$

giving

$$\text{VA}_{\text{H}} = 23.58 \text{ \$}/\text{Mscf or } 18.67 \text{ \$}/\text{kmol}$$

The hydrogen consumption is fixed in this case, and there is no economic return on using more hydrogen, so the value added is constant and is plotted as a straight line of length 0.152 kmol/s in Figures 10 and 11. If the product spectrum varied with hydrogen consumption (as is the case in hydrocracking) then the calculation would be repeated at different levels of hydrogen consumption to generate a curve.

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Received for review June 14, 1995

Revised manuscript received March 27, 1996

Accepted March 27, 1996*

IE950359+

* Abstract published in *Advance ACS Abstracts*, May 15, 1996.