

Alternative technologies to steam-methane reforming

Consider these different processes to produce hydrogen and carbon monoxide

B. M. Tindall and M. A. Crews, Howe-Baker Engineers, Inc., Tyler, Texas

Steam-methane reforming (SMR) has been the conventional route for hydrogen and carbon monoxide production from natural gas feedstocks. However, several alternative technologies are currently finding favor for an increasing number of applications. The competing technologies include:

- Steam-methane reforming combined with oxygen secondary reforming (SMR/O₂R)
- Autothermal reforming (ATR)
- Thermal partial oxidation (POX).

Each of these alternative technologies uses oxygen as a feedstock. Accordingly, if low-cost oxygen is available, they can be an attractive alternate to SMR with natural gas feedstocks. Low-cost oxygen is now available in many large industrial sites where a large air separation plant already exists or can be economically installed. (Note that, unlike ammonia plant technology, air cannot be used in place of oxygen since the nitrogen would dilute the hydrogen/carbon monoxide product.)

SMR. This technology essentially consists of a fired heater containing catalyst-filled tubes (Fig. 1). Steam is added to the natural gas feedstock. The mixture is then preheated to about 1,050°F and passed through catalyst tubes. The catalyst converts the gas mixture to hydrogen, carbon monoxide and carbon dioxide. The reaction is endothermic, with heat supplied by burners located adjacent to the tubes. The reaction mixture exits the reformer at about 1,600°F. Combustion gas heat is recovered in the convection section. A more detailed SMR description and process parameters associated with its design are described by Tindall and King.¹

SMR/O₂R. This essentially consists of an SMR followed by an oxygen secondary reformer (Fig. 2). The oxygen reformer is a refractory-lined vessel containing catalyst and a burner. The SMR reaction mixture is fed to the oxygen reformer's top where it is mixed with oxygen fed through the burner. Partial oxidation reactions occur in

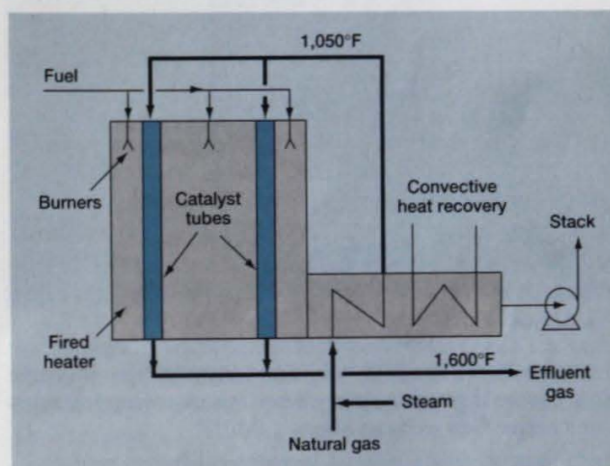


Fig. 1. Typical SMR.

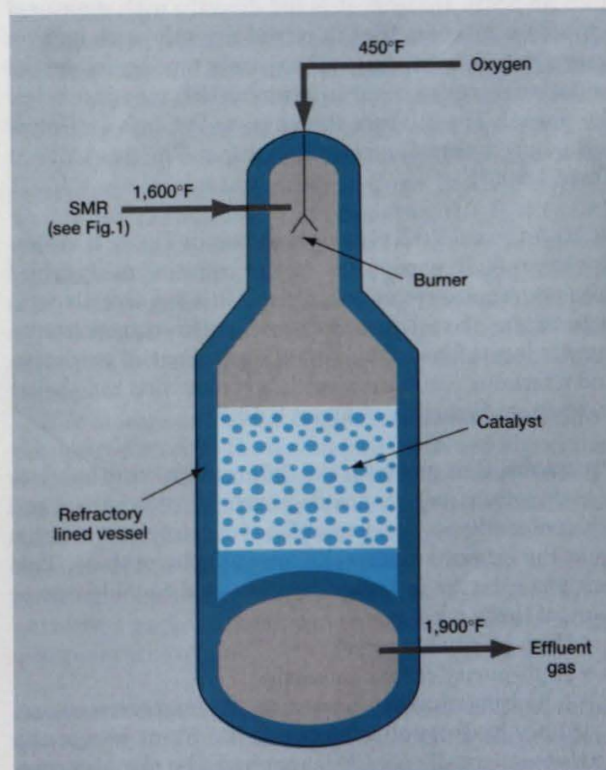


Fig. 2. Typical SMF/O₂R.

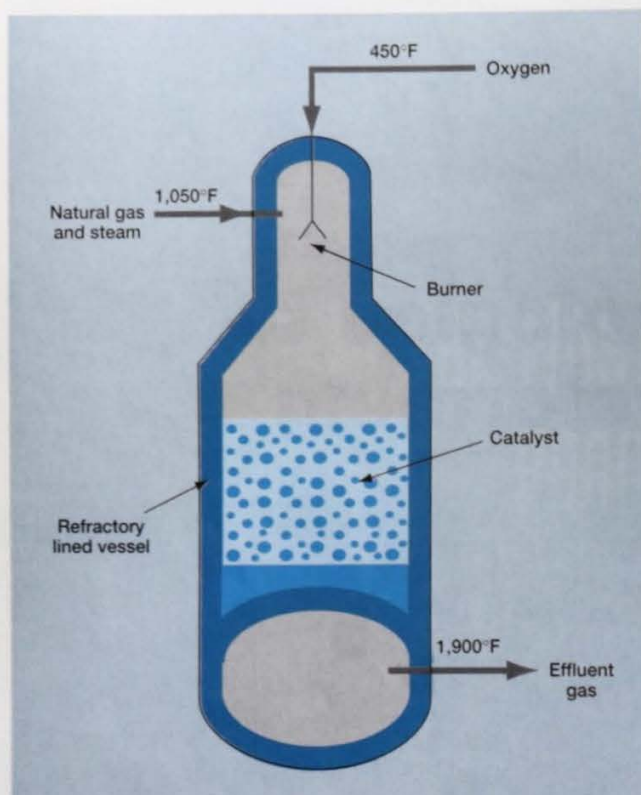


Fig. 3. Typical ATR.

a combustion zone just below the burner. The mixture then passes through a catalyst bed where reforming reactions occur. Gas exits at about 1,900°F.

ATR. A typical ATR is shown in Fig. 3. It is similar to an oxygen secondary reformer except it does not receive feed from an SMR. Instead, it is fed directly with a natural gas/steam mixture that is mixed directly with oxygen from a burner located near the vessel's top. Again, partial oxidation reactions occur in a combustion zone just below the burner. The mixture then passes through a catalyst bed where reforming reactions occur. The gas exits at about 1,900°F.

POX. A typical POX reactor is shown in Fig. 4. It is similar to an ATR, except it does not contain catalyst and does not require steam in the feed. It is fed directly with natural gas that is mixed directly with oxygen from a burner located near the vessel's top. Partial oxidation and reforming reactions occur in a combustion zone below the burner. Gas exits at about 2,500°F.

Products. Exit gas from the different reactors consists of hydrogen, carbon monoxide, carbon dioxide, steam and residual methane. Small quantities of nitrogen and argon from the original feedstocks may also be present. This exit gas mixture is typically processed to yield one or more of these products:

- High-purity hydrogen
- High-purity carbon monoxide
- A hydrogen/carbon monoxide gas mixture.

If only hydrogen is required, the plant becomes a hydrogen plant. If only CO is required, the plant becomes a carbon monoxide plant. If both hydrogen and carbon

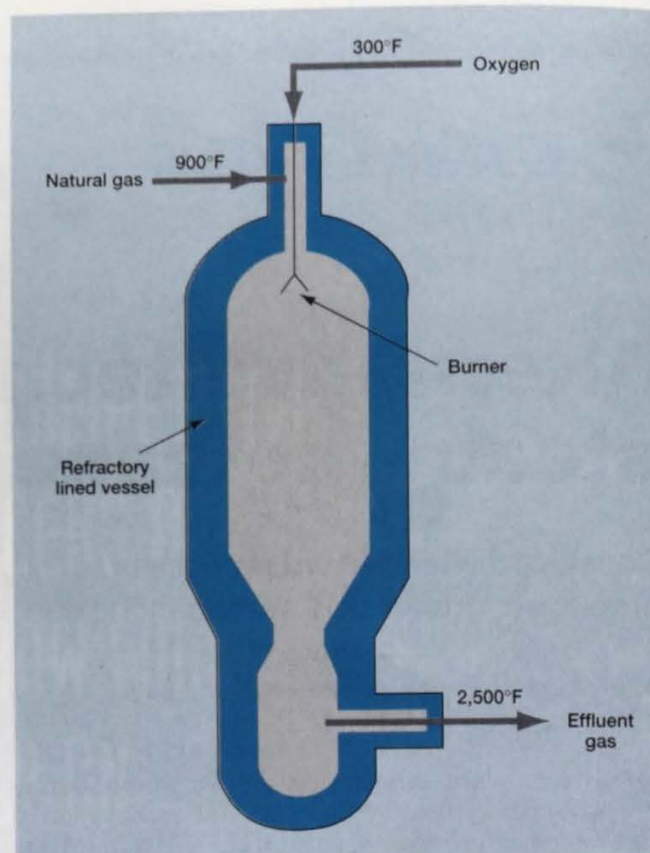


Fig. 4. Typical POX.

monoxide are required as separate streams, the plant is typically known as a HYCO plant. If only a hydrogen/carbon monoxide mixture is required, the plant is typically known as a synthesis gas (or syngas) plant. And if all three products are required, the plant is considered a combination (hydrogen/carbon monoxide/syngas) plant.

H₂/CO ratio. A key variable in the design of these plants is the product H₂/CO ratio. For HYCO and syngas plants, the product H₂/CO ratio typically varies from 1.0 to about 3.0. But for hydrogen plants, the ratio is almost infinite. And for carbon monoxide plants, the ratio is essentially zero.

Natural ratio range. Each technology produces inherently different H₂/CO ratios. The natural ratio range is defined as the range of ratios that can be achieved by varying only the CO₂ recycle. Natural ratio ranges for each technology are shown in Fig. 5, as applicable to natural gas feedstocks. Other feedstocks will produce a different set of natural ratios. As seen in Fig. 5, ranges for natural gas are as follows: SMR—3.0 to 5.0; SMR/O₂R—2.5 to 4.0; ATR—1.6 to 2.65; POX—1.6 to 1.8.

Note that some ranges are broader than others and that some ranges do not overlap. The technology that offers a natural ratio that spans the required product ratio is considered to have an inherent advantage and merits careful consideration.

CO₂ recycle is the typical means of tailoring the natural ratio span to meet a desired H₂/CO product requirement. As noted earlier, CO₂ is present in all reactor effluents. Since CO₂ is considered an impurity, it must typically be eliminated. In most designs, CO₂ is removed from the process gas by selective adsorption in a suit-

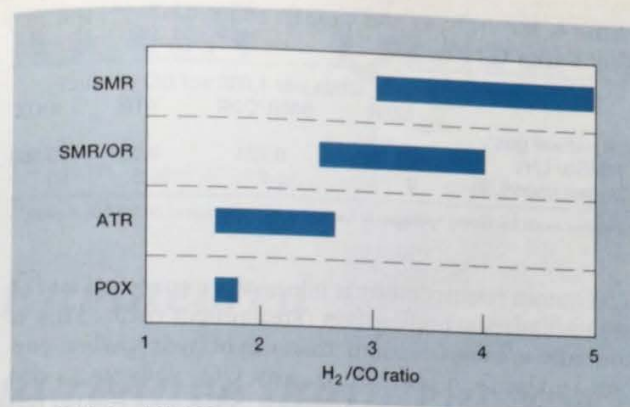


Fig. 5. Natural H₂/CO ranges for natural gas feed.

able solvent, such as an amine solution. CO₂ is then stripped from the solvent as a separate stream. (Synthesis gas for methanol plants typically retains some or all CO₂. This is a special case that is outside the scope of this article.)

The separate CO₂ stream can be removed from the system or recycled to the reactor. If it is recycled, CO₂ can be converted to CO in the reactor by the reverse water-gas shift reaction. This reduces the final H₂/CO ratio because carbon atoms in the original CO₂ are converted to CO. On the other hand, if CO₂ is not recycled, the H₂/CO ratio increases because the carbon atoms in the original CO₂ are not converted to CO. (CO₂ that is not recycled is typically vented to the atmosphere; however, sometimes it is sold as a byproduct.)

The natural H₂/CO range for each technology represents the spread between full CO₂ recycle and no CO₂ recycle. By operating with partial recycle, any H₂/CO ratio within the natural range can be achieved. But as noted earlier, some of the natural ratio ranges do not overlap. Hence, for a given product H₂/CO ratio, at least some of the technologies will require additional ratio adjustment to meet product requirements. Fortunately, a number of process techniques are available to do this. The technology's viability will depend on the economics of using these techniques.

Common techniques for decreasing the ratio below its natural range include importing CO₂, using a membrane or using a cold box. To increase the ratio, common techniques include increasing steam in the reactor feed or adding a shift converter. These techniques, along with CO₂ recycle, are summarized in Table 1.

Import CO₂. The H₂/CO ratio can be decreased by importing CO₂ as reactor feed. Import CO₂ is added to the CO₂ already being recycled. The carbon atoms in the import CO₂ can then be converted to CO by the reverse water-gas shift reaction.

Membrane. The H₂/CO ratio can also be decreased by using a membrane unit. Hydrogen is removed from the membrane as a permeate stream, which reduces the H₂/CO ratio of the main process stream.

Cold box. This is often used to separate hydrogen and carbon monoxide into a high-purity CO stream and an H₂-rich stream. This reduces the ratio to near zero with respect to the CO stream. The H₂-rich stream may undergo further purification (typically in a PSA unit) to yield a high-purity H₂ stream. This increases the ratio to near infinity with respect to the H₂ stream.

Table 1. Techniques for H₂/CO ratio adjustment

	Decreases ratio	Increases ratio
Recycle CO ₂	X	
Import CO ₂	X	
Use membrane	X	
Remove CO ₂		X
Increase steam		X
Add shift converter		X
Use cold box	see note	

Note: A cold box decreases the ratio with respect to CO and increases the ratio with respect to H₂.

Table 2. H₂/CO ratio summary, natural gas feed

	Import CO ₂ or membrane	Total CO ₂ recycle	No CO ₂ recycle	Increase steam	Add shift converter
SMR	<3.0	3.0	5.0	>5.0	-infinity
SMR/O2R	<2.5	2.5	4.0	>4.0	>5.0
ATR	<1.6	1.6	2.65	>2.65	>3.0
POX	<1.6	1.6	1.8	>1.8	>2.0

Blue letters show the natural ratio range.

A cold box can also be used. It can reduce the ratio to essentially zero with respect to CO. And in combination with a PSA unit, it can increase the ratio to near infinity with respect to H₂.

Steam. Adding steam to the reactor converts CO to H₂ by the water-gas shift reaction, which increases the H₂/CO ratio.

Shift converter. This is a catalytic reactor that catalyzes conversion of CO to H₂ by the water-gas shift reaction. This step can be used to increase the H₂/CO ratio to a very high value. It is widely used in hydrogen plants.

Table 2 summarizes the ranges achievable by each technology by using these techniques. Typically, the technology's viability decreases with the magnitude of the added steps necessary to achieve a required product H₂/CO ratio.

Other considerations. As previously stated, these ratios are based on natural gas feedstocks. If heavier feedstocks are used, the ratios will be lower because the feed hydrogen-to-carbon ratio will be lower.

The above ratios are based on typical reformer outlet temperatures and pressures for each technology. Reformer outlet temperatures are typically set by the residual methane requirement. Reformer outlet pressures are typically set by compression requirements. Some design flexibility often exists between these limits. However, within the normal range of flexibility, the H₂/CO ratio does not change appreciably with reformer outlet temperature or pressure. Hence, for a given design, it is normally impractical to achieve a significant change in H₂/CO ratio by varying reformer outlet temperatures or pressures. Instead, the techniques discussed above should be used.

If it is impractical for a given technology to achieve the desired ratio by the techniques discussed above, then excess H₂ or CO can be burned as fuel in the SMR (for SMR and SMR/O2R plants) or in the process heater (for ATR or POX plants). If necessary, the process heater can be expanded to include a second radiant section to permit burning of excess product by generating steam. Alternatively, a package boiler can be used to burn excess gas and generate steam.

Comparisons. Table 3 is a comparison of key process advantages and disadvantages for the technologies under consideration for hydrogen/carbon monoxide plants with natural gas feedstocks. Note that while the oxygen

requirement is shown as a disadvantage, it may not be in cases where low-cost oxygen is available.

Process parameters. Key process parameters and feedstock requirements for each technology include pressure, temperature, steam/carbon ratio, methane slip, raw materials and export steam.

Pressure. Most SMR plants run at reformer outlet pressures between 150 and 400 psig. The maximum pressure is about 500 psig, due to metallurgical considerations in the SMR outlet piping. The same applies to SMR/O₂R plants. This limits the final product gas pressure to about 450 psig. Above this, product gas compression is required. ATR and POX plants can run at much higher pressures. For example, some plants require synthesis gas at about 800 psig, which can be supplied directly from an ATR or POX without synthesis gas compression.

Temperature. SMR plants typically run at reformer outlet temperatures of 1,550°F to 1,600°F. SMR/O₂R and ATR plants typically run at outlet temperatures of 1,750°F to 1,900°F. And POX plants typically run at about 2,500°F. The high POX temperature is needed to maintain low residual methane without any catalyst.

Steam/carbon ratio. Steam is typically required to prevent carbon formation on the reformer catalyst.

Table 4. Natural gas and oxygen requirements, U.S. Gulf Coast CO plant

	Units per 1,000 scf CO product			
	SMR	SMR/O ₂ R	ATR	POX
Net natural gas*, MMBtu LHV	0.729	0.724	0.531	0.509
Oxygen import, lb	0	14.2	56.5	58.7

* Includes credit for excess hydrogen at fuel value. All cases based on full CO₂ recycle.

The steam requirement is generally expressed as the steam/hydrocarbon-carbon (steam/hcc) ratio. This is the ratio of moles of steam to moles of hydrocarbon-carbon in the feed (carbon in any CO₂ recycle is not included in the ratio calculation). SMR and SMR/O₂R plants typically use a 3/1 steam/hcc ratio for no CO₂ recycle and a 2/1 ratio when all the CO₂ is recycled. A lower ratio can be used with CO₂ recycle since the CO₂ makes some H₂O by the water-gas shift reaction. For partial recycle, a ratio between 3/1 and 2/1 is typically used.

ATR plants can operate at a lower ratio, often about 1.35, with or without CO₂ recycle. POX plants require no steam. Some POX soot is formed, but since there is no catalyst, there is no possibility of catalyst bed plugging. With proper design and operation, soot can be processed and removed in the downstream equipment with-

Table 3. Process technology comparison, natural gas feed

Advantages	Disadvantages
SMR 1. Largest number of units in commercial operation; more industrial experience. 2. Does not require oxygen. 3. Reforming step runs at lowest process gas outlet temperature (~1,600°F). 4. Best natural H₂/CO ratio (3 to 5) if only hydrogen is to be produced.	1. Natural ratio is higher than typically required when carbon monoxide is also to be produced. 2. Highest atmospheric emissions.
SMR/O₂R 1. O₂R outlet gas contains less residual methane than SMR. Favors plants with higher syngas purity requirements. 2. Reduces size of SMR. 3. Methane content of process gas can be tailored (by adjusting O₂R outlet temperature) to meet downstream process requirements (for example to satisfy a methane-wash cold box material balance or to more closely match a methane impurity spec in a syngas product).	1. Requires two-step reforming. 2. Operates at higher process gas outlet temperature than SMR. 3. Requires oxygen.
ATR 1. Natural H₂/CO ratio is often favorable (1.6 to 2.65). 2. Runs at lower outlet gas temperature than POX. 3. Low residual methane in process gas. 4. Methane content of process gas can be tailored (by adjusting ATR outlet temperature) to meet downstream process requirements (for example to satisfy a methane-wash cold box material balance or to more closely match a methane impurity spec in a syngas product).	1. Limited commercial experience. 2. If total CO₂ recycle is required, the corresponding CO₂ recycle rate is much higher than POX. 3. Requires oxygen.
POX 1. Does not require feedstock desulfurization. This is more a difference than an advantage, since the sulfur must eventually be removed anyway. 2. Does not require steam. Since there is no catalyst bed, carbon formation can be tolerated, and so a POX is typically operated without steam. This significantly lowers the CO₂ content of the reactor exit gas. 3. Residual methane in process gas is very low (typically 0.3 mol pct max, dry basis). 4. Natural H₂/CO ratio is inherently low (1.6 to 1.8). Therefore, an advantage if the required ratio is low.	1. Natural H₂/CO ratio is inherently narrow (1.6 to 1.8). Disadvantage if the required ratio is above about 2.0. 2. Reforming step operates at very high temperature (~2,500°F). 3. Methane content of process gas is inherently low and cannot easily be tailored to meet downstream process requirements. 4. Requires oxygen. 5. Makes carbon (soot). 6. Requires complex heat recovery section to handle the high temperature and the soot. 7. Licensed process with royalty and significant third party involvement.

out affecting the plant onstream time.

Methane slip. Exit gas from each reactor contains some residual methane from unreacted natural gas feed. This is typically referred to as methane slip. A low methane slip increases the synthesis gas product purity. It also reduces the natural gas requirement. SMRs typically have a relatively high methane slip (3 to 8 mol%, dry basis). This is primarily because the SMR operates at a lower outlet temperature. Other technologies operate at higher outlet temperatures and generally have low slips (0.3 to 0.5 mol%, dry basis).

If a methane-wash cold box is used, typically a methane slip of at least 1 to 2 mol% is required to maintain the box's methane level. This is not a problem for an SMR design because its methane slip is considerably more than this. It is also easily achieved by the SMR/O₂R and ATR designs by simply reducing the reactor outlet temperature. However, this methane level is more difficult to achieve with a POX, since, in the absence of a catalyst, a high temperature and a corresponding low methane slip should be maintained to ensure consistent performance.

Raw materials. Natural gas and oxygen are the two major raw materials. For each technology, the quantities required must be considered on a case-by-case basis, since they depend on the H₂/CO requirement for each application. For example, the product H₂/CO ratio may require that CO₂ be recycled or vented, depending on the ratio and technology. If the required H₂/CO product ratio is 2.0, then all the CO₂ is recycled in an SMR or SMR/O₂R design (Fig. 5), part of the CO₂ is recycled in an ATR design and no CO₂ is recycled in a POX design.

The extent of CO₂ recycle changes the raw material requirements for a given technology, because, if CO₂ is vented, its contained carbon and oxygen are not recovered.

To provide a basis of comparison, a design can be considered where all the CO₂ is recycled for each technology. Referring to Fig. 5, this would normally occur for designs for a H₂/CO product ratio less than 1.6. A typical design meeting this requirement would be a CO-only plant (H₂/CO ratio of zero). For such a design, we have recently compared all four technologies for a proposed U.S. Gulf Coast plant. For this plant, natural gas and oxygen requirements are in Table 4. The natural gas requirement shown is the net requirement on a heating value basis and includes credit for excess hydrogen at fuel value. (For this plant, all the technologies produce excess hydrogen since CO is the only required product and there is no requirement for product hydrogen.)

For simplicity, SMR and SMR/O₂R are referred to as SMR-based technologies because the SMR is the dominant component. ATR and POX are called oxygen-based technologies because the partial oxidation reactor is the dominant component. From Table 4, note that natural gas requirements for SMR-based technologies are about the same. Note also that natural gas requirements for oxygen-based technologies are about the same. However, the oxygen-based technologies require only about 70% as much natural gas as the SMR-based technologies.

The natural gas requirement is lower for oxygen-based technologies because most of the oxygen in the feed reacts

with carbon in the natural gas to form carbon monoxide. The oxidation reaction is, therefore, more efficient for the formation of carbon monoxide, which is the desired product for this plant.

Another reason for the lower natural gas requirement is that, for the oxygen-based technologies, required heat for reaction is applied directly to process gas in the reactor vessel. This is more energy efficient than the SMR-based technologies, which require a temperature driving force between the combustion gas and the in-tube process gas.

With respect to oxygen consumption, the oxygen requirement for the SMR is obviously zero. For the SMR/O₂R, the oxygen requirement is about 25% of that for the ATR or POX. The ATR and POX oxygen requirements are about the same. This is expected since both technologies use the same direct combustion process and, for the example plant, both technologies recycle all the CO₂ and produce essentially the same H₂/CO product ratio.

Export steam. For the example plant, export steam is relatively low since excess hydrogen is not burned within the plant to make export steam. Accordingly, export steam for the SMR, SMR/O₂R and POX averaged only about 150 lb per 1,000 scf of CO and any differences were not considered significant. However, the ATR export steam was less than half this value because the energy requirement for the CO₂-removal system is larger.

Economic considerations. The economics of each technology depend on the conditions and requirements of each project, and must be studied on a case-by-case basis. Some of the more important considerations follow.

Oxygen availability. The availability of oxygen is obviously a key parameter. Since the SMR requires no oxygen, it is the obvious choice if oxygen is unavailable or prohibitively expensive. Studies indicate that oxygen-based technologies can be attractive if oxygen is available at less than about \$25/short ton. If oxygen costs more than about \$30/ton, SMR is favored. The oxygen price can be less than \$25/ton in large industrial sites where a large air separation plant already exists or can be economically installed to serve the area's needs. Hence, in such cases, oxygen-based technologies merit serious consideration.

Hydrocarbon feedstock. With natural gas, all technologies are technically viable. However, if the feedstock is a heavy hydrocarbon (such as fuel oil or vacuum bottoms), POX is the only viable technology. This is because the other technologies cannot process feedstocks heavier than naphtha (to avoid carbon deposition on the catalyst).

H₂/CO ratio. The importance of the product H₂/CO ratio has already been extensively discussed. As previously stated, the technology that offers a natural ratio spanning the required product ratio has an inherent advantage and must be seriously considered.

Natural gas price. Since SMR-based technologies directionally require more natural gas, they are favored by low natural gas prices.

Capital cost. SMR-based technologies typically have a higher capital cost. This is because the SMR furnace, with its high-alloy tubes and large flue-gas heat-recovery section, is inherently more expensive than ATR or POX

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technologies which are refractory-lined carbon-steel vessels without external flue-gas heat recovery.

An SMR has a lower capital cost than an SMR/O₂R when the operating pressure is relatively low. At low pressure, most of the reforming occurs in the SMR, and the O₂R does not significantly reduce the SMR's size. But at higher pressures, an SMR/O₂R can cost less, because more of the reforming is done in the O₂R, and the SMR's size can often be significantly reduced.

ATR and POX technologies have offsetting capital costs, depending on the extent of CO₂ recycle. For full CO₂ recycle, the CO₂ removal system is much larger for the ATR than the POX and the added capital cost associated with this difference tends to make the ATR more expensive. However, for no CO₂ recycle, the ATR tends to cost less than the POX because its reactor and heat-recovery section are inherently less expensive, and it does not carry any third party royalty.

Based on the above, the following conclusions can be drawn:

1. The SMR/O₂R, ATR and POX technologies can be attractive if low-cost oxygen is available.
2. For competing technologies, the H₂/CO product ratio is typically the most important process parameter.
3. For low methane slip, the SMR/O₂R, ATR and POX technologies are favored.
4. For full CO₂ recycle, POX is usually better than ATR.
5. Relative to POX, the ATR is a nonlicensed technology that avoids third-party involvement.
6. Economics of each technology are dependent on the conditions and requirements for each project and must be evaluated on a case-by-case basis.

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The authors

Bob Tindall is the manager of process engineering, syngas division, for Howe-Baker Engineers, Inc., Tyler, Texas. He has over 30 years experience in process design, first with C. F. Braun & Co., Alhambra, California, primarily with ammonia and hydrogen plants. For the last 20 years, he has worked for Howe-Baker, primarily with hydrogen, carbon monoxide and synthesis gas plants. He received his BS degree in chemical engineering from the University of Arkansas and his MS and PhD degrees in chemical engineering, both from the University of Southern California. He is a licensed professional engineer in California and Texas.

Andy Crews is a process engineer, syngas division, for Howe-Baker Engineers, Inc., and is responsible for the process design of hydrogen, carbon monoxide and synthesis gas plants. Other responsibilities include design, modification and maintenance of Howe-Baker's inhouse process design software. He holds AS and BS degrees from the University of the State of New York, and an MS degree in chemical engineering from the University of Arkansas.

