ECONOMIC ANALYSIS OF VARIOUS REFORMING TECHNIQUES AND FUEL SOURCES FOR HYDROGEN PRODUCTION

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A Thesis
Submitted to
the Graduate Faculty of
Auburn University
in Partial Fulfillment of the
Requirements for the
Degree of
Master of Science

Auburn, Alabama
December 15, 2006

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THESIS ABSTRACT

ECONOMIC ANALYSIS OF VARIOUS REFORMING TECHNIQUES AND FUEL SOURCES FOR HYDROGEN PRODUCTION

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Master of Science, December 15, 2006
B.ChE., Auburn University, 2004

102 Typed Pages

Directed by Mario Richard Eden

Hydrogen is emerging as a future replacement fuel for the traditional fossil fuels that will be capable of satisfying our energy needs. Hydrogen may enable future energy systems to be cleaner, more reliable, and much more efficient; thus possibly ensuring our energy security and environmental viability. One of the many major challenges of a future hydrogen energy economy is the reduction in the cost of production, storage, and transportation of hydrogen.

A generic, robust optimization framework has been developed that enables the identification of economically optimal hydrogen production schemes. Inclusion of constraints on capacity, fuel complexity, and capital investment has been successfully tested for linear and non-linear functions. In this work a total of 16 rigorous process simulation models have been developed for multiple reformation strategies; steam reformation (SR), partial oxidation (POX), auto thermal reformation (ATR), supercritical methanol reformation (SC), and dry methane reformation (DR). The various hydrogen production schemes were investigated for three different fuels: natural gas (approximated by methane), diesel (approximated by dodecane), and methanol. The models included all the feed pretreatment steps along with the reforming reactors and effluent treatment including the water gas shift reactors. Using process integration techniques and advanced computer-aided tools, the systems have been optimized and the economic potential of the technologies evaluated. This work provides a comparison of reformation strategies based on their utility requirements, effects of fuel complexity, energy integration potential, size constraints, electricity production capabilities, and economics; challenging previous ideas on how to compare the efficiency and economic feasibility of each reformation strategy.

The results obtained in this work indicate that for industrial scale production of hydrogen, only dry reforming (DR) of natural gas shows any promise for competing with the traditional reforming strategies like steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). For size-constrained systems, e.g. onboard vehicular fuel processing systems, partial oxidation appears to provide the best trade-off between power production and system size.

ACKNOWLEDGMENTS

The author would like to thank Dr. Mario R. Eden for his guidance and mentoring throughout my college and graduate careers. He has not only been a great teacher, but also a great friend. Thanks to my parents, Charles and Brenda McGlocklin, and my grandparents, Mac and Rosetta Landers and Mamie McGlocklin, for their love, encouragement and faith in me, without which this thesis would not have been completed. Thanks are also due to my friends and co-workers Fadwa Eljack, Ahmed Abdelhady, and Norman Sammons for their support during the last two years of working on this project. Also I would like to thank Rose Cummings for fruitful collaboration on parts of this project and for her contributions, particularly to the aspects of process integration under size constraints. Finally, I want to acknowledge the financial support for this project provided by the Department of Energy – National Energy Technology Laboratory and the Consortium for Fossil Fuel Science (CFFS).

Style manual or journal used: *Computer-Aided Chemical Engineering*

Computer software used: Microsoft Windows XP

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1. INTRODUCTION

Energy systems of the future will need to be cleaner, more reliable, and much more efficient to ensure our energy security and environmental viability. Hydrogen is a potential answer to satisfying many of our energy needs, and considered to be one of the best candidates for replacing fossil fuels. The sale of hydrogen has increased 6% annually in the last five years. (U.S. Department of Energy, 2004) This is largely due to an increased use of hydrogen in oil refineries, which is a result of stricter regulations on the quality of fuels. Using hydrogen as a source of energy is not a new idea. Hydrogen has been used domestically and in industrialized processes for many years. Current interests in producing hydrogen for energy arises from today's environmental and energy policies concerning climate change, air pollution, energy supply security, and breakthroughs in fuel cell technology. Furthermore, the integration potential of a fuels processing system is inherently large, in terms of both energy and material recovery (Godat et al., 2003). The transition to a hydrogen economy will progress through multiple production processes and will eventually evolve into sustainable production. The reality is that while a growing hydrogen economy already exists in the chemical and refining industries, a much greater one is to come.

The objective of this work is to develop process simulation models of various fuel reforming strategies, generate the data required for subsequently performing thermal pinch analyses, evaluate the integration potential of the processes to identify potential energy savings, and generate production cost reports for each reforming method based on specific hydrocarbon fuels. Several reforming strategies will be evaluated to compare energy and cost savings. Also various hydrocarbon fuels will be investigated to observe how fuel complexity affects integration potential and overall production costs. The main goal of this work is to determine which combination of reforming strategy and hydrocarbon fuel is the most effective and cost efficient for a given application.

2. BACKGROUND

2.1. Environmental Effects

A future hydrogen economy would significantly reduce air, water, and soil pollution; along with reducing the irreversible effects of climate changes. The burning of fossil fuels generates emissions to the air, while a wide variety of other energy production and consumption processes deliver direct emissions to the water and soil.

There are three major generation sources that release emissions into the air. The generation sources are as follows: stationary combustion, mobile applications, and processing. Stationary combustion is responsible for emissions released due to burning of fossil fuels in different types of stationary applications, such as gas turbines. Mobile applications, such as automobiles, are accountable for any emissions released from forms of transportation. Finally, processing is responsible for all emissions released that are not caused by combustion, such as waste disposal processes.

The three main emissions that are released to the environment are carbon dioxide (CO_2), nitrogen oxides (NO_x), and non-methane volatile organic compounds (NMVOC). Carbon dioxide is formed through combustion of fuels that contain carbon, while nitrogen oxides (NO, and NO_2) are both formed during the combustion process. When these compounds are released into the atmosphere, they react with sunlight and cause smog. Vast ecosystem damage and increased potential for human cancer development are just some of the examples of the ultimate prices that are being paid for consuming these fossil fuels.

To avoid irreversible changes in the climate, the United Nations panel on climate change (IPCC) has estimated that global CO_2 emissions will have to be reduced 50-60% over the next 100 years (U.S. Department of Energy, 2004). If we continue to burn fossil fuels at our present rate, we could experience a quadrupling of world CO_2 emissions over the course of the next 125 years as a consequence of population growth and increased energy demands. (Lindebe, 1998)

To achieve this goal, while allowing developing countries a certain percentage increase, already developed countries will have to decrease their emissions considerably. The use of cleaner fuels will help meet our environmental needs. The use of hydrogen will reduce carbon dioxide and other greenhouse gas emissions by utilizing the three-fold increase in thermal efficiency.

Energy production must also become cleaner and more efficient to avoid permanent damage to our environment, caused by the burning of fossil fuels. Hydrogen production from fossil fuels affects the environment, by depleting natural resources and releasing carbon dioxide emissions. Energy needs are constantly increasing due to population and industrial growth. However, there is no immediate replacement for all forms of fossil fuels, given that 90% of the world's hydrogen production comes from the processing of fossil fuels. Since fossil fuels can not be immediately replaced, the decision must be made on how to utilize the qualities of the different fossil fuels. There are four important factors to take into account when choosing which fossil fuel is best for a certain application, they are as follows: physical properties, energy content, environmental consequences, and economics.

The physical properties of the fuels have a significant impact on the amount of useful energy that can be produced from each type of fossil fuel. For example coal in solid form provides the best longterm hydrogen storage, while liquid fuels provide the best transportation capabilities and also high hydrogen content. Natural gas has the highest hydrogen content, but is not feasible for transportation fuels.

The future growth potential of each energy source is primarily dependent on their energy content. The larger the percentage concentration of hydrogen, the greater the energy content of that fossil fuel.

Environmental impact is vastly dependent on the chemical makeup of the fuel. When looking at CO_2 emission; the higher the carbon concentration in the fuel the more CO_2 is produced by combustion. Since all processes ultimately have an impact on the environment, it is extremely important that all energy is used efficiently. To ensure that the energy is being used efficiently, processes should consume the least amount of energy that is technically possible. For a process to be environmentally efficient it should be using clean energy of the right quality effectively.

There is no short-term solution, but by converting fossil fuel sources into hydrogen and electricity we can address the energy needs while reducing CO_2 emissions.

2.2. Hydrogen as a Primary Energy Carrier of the Future

The concept of a future hydrogen economy will use hydrogen as the main energy carrier, thus possibly creating a reliable and sustainable energy supply system. Once the hydrogen energy economy infrastructure is established, it will be easy to identify the benefits of using hydrogen as our main energy carrier. Current energy carriers are petroleum based fuels, and when they are burned with oxygen they produce carbon dioxide, a primary greenhouse gas, and carbon monoxide, which is poisonous.

Some of today's energy carriers are electricity, gasoline, diesel fuel, and natural gas. These carriers are made by the conversion of primary energy sources, such as coal, petroleum, and underground methane, into an energy form that is easily transported and delivered in a usable form to industrial, commercial, residential, and transportation end-users. Electricity and hydrogen are proposed as the dominant energy carriers of the future sustainable energy supply system. The first step toward the path of a future hydrogen energy economy is using readily available energy sources for the production of hydrogen. Some readily available resources include: coal, oil, and natural gas.

Since hydrogen is found in nature only as part of other compounds, it must first be converted to elemental hydrogen (H_2) through the use of energy, before hydrogen itself becomes available as a fuel. This implies that hydrogen is an energy carrier, not an energy source. Hydrogen is able to store and deliver energy in a usable form, but first it must be produced from compounds that contain it. There are a variety of primary energy sources and feed stocks with related technologies for hydrogen production; where the feedstock primarily dictates the choice of production method. Primary energy production presently means hydrogen production from fossil fuels via natural gas reforming as well as the partial oxidation of heavy fuel oil (or diesel) and coal. Along with these further processes are in the research and development phases.

When consumers receive energy from fossil fuel energy sources, it is usually delivered in the form of different energy carriers. For example, oil is refined into energy products such as gasoline or diesel fuel.

The production, transportation, and storage of hydrogen in a cost effective, environmentally friendly manner are one of the major challenges to the development of the hydrogen economy. Hydrogen has the highest energy content per unit weight of known elements (U.S Department of Energy, 2004), however hydrogen has a low volumetric energy density. Hydrogen's low energy density presents challenges to transporting, delivering, and storing large quantities of hydrogen.

There are two fundamental questions that first must be addressed before a hydrogen infrastructure can be put in place. First, how much energy is required to extract hydrogen from hydrogen-rich, naturally occurring compounds? Second, should hydrogen be produced at large scale centralized locations, and then stored and transported to the end users or small scale decentralized locations, produced on-site or closer to the point of use? Decentralized production of hydrogen allows for smaller capital investments and minimal transport and delivery infrastructures. However, centralized production of hydrogen enables production on a much larger scale. More research and development will be needed to lower the cost of transporting and storing hydrogen. Developing the infrastructure necessary to produce, store, and deliver the large quantities of hydrogen necessary for the future of the hydrogen energy economy is one of the major challenges.

2.3. Reformation Strategies

2.3.1. Introduction

The amount of fossil fuel resources is limited; however, this is not the case with hydrogen as it can be produced from renewable resources. We currently consume fossil fuels 100,000 times faster than they are made, thus leading to questions about how long our worldwide supplies will last (U.S. Department of Energy, 2004). Hydrogen can be produced from hydrocarbon fuels, such as coal, oil, and natural gas, through the process of reformation. During the combustion process, hydrogen binds itself to oxygen for the air and produces water; therefore hydrogen is completely renewable. Since hydrogen can be obtained from renewable resources unstable production will no longer be a concern.

Reformation is the conversion of hydrocarbon based fuels to a gaseous mixture that contains hydrogen. Through various reformation strategies, sufficient hydrogen can be produced for various fuel cell applications and electrical power. Hydrogen can be derived from hydrocarbons through various process techniques. The U.S. currently produces over 9 million tons of hydrogen annually (Bellona, 1999). Steam reforming (SR), partial oxidation reforming (POX), auto thermal reforming (ATR), supercritical methanol reforming (SC), dry methane reforming (DR), and electrolysis are the most investigated reforming strategies, and are believed to be the key aspects of the potential development of the future hydrogen energy economy.

2.3.2. Steam Reforming

Steam reforming is the most common and technically well-proven industrial reformation strategy; in addition, it has the highest hydrogen yield of all reforming strategies. Most of the industrial hydrogen in the United States is produced by steam reforming in the chemical manufacturing and petroleum industries. The industrial scale production of hydrogen is carried out in steam reforming plants with usual capacities in the order of 100,000 Nm^3/hr. (Bellona, 2004)

Steam reforming of natural gas is currently the least expensive method of hydrogen production, and accounts for 95% of the hydrogen that is produced worldwide today. Steam reforming of natural gas offers an efficient, economical, and widely used process for hydrogen production, and provides near and mid-term energy security and environmental benefits. Steam reforming exhibits the highest efficiencies of current economically available production methods; around 65% to 70%. Research has shown that with higher thermal integration the production efficiency could increase to over 85% (NYSERDA, 2003). To realize this integration potential, the remaining fuel in the waste gas is burned and the heat generated is then recycled back to the reactor.

Steam reformers can use natural gas and light hydrocarbons to produce hydrogen. The reaction that occurs during this type of reformation is highly endothermic, and thus requires a significant source of heat. Industrial steam reforming processes are normally carried out at temperatures between 700 and 1100ºC and pressures between 3 and 25 bar. The fuel is vaporized and fed with steam to the reactor, where the reaction generates carbon monoxide and hydrogen.

$$C_nH_m + nH_2O \;\rightarrow\; nCO + \left(n + 0.5m\right)H_2 \qquad (1)$$

The second step in the reformation process is the exothermic water gas shift reaction (WGS), which reacts carbon monoxide with additional steam to produce more hydrogen and carbon dioxide. This reaction does not decrease the levels of carbon monoxide enough for some hydrogen fueled applications like Proton Exchange Membrane (PEM) fuel cells; requiring further post reformation clean up steps.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

Steam to carbon molar ratio, system pressure, and heating requirements are the primary factors that influence the reaction rate. Reaction kinetics usually determine the design of the reactor; however, since the combined process reactions are still endothermic the reactor design is more dependent on the heat transfer capabilities of the system. Traditionally, combustion of part of the fuel is used to preheat feeds and externally heat the reactor (Zale et al., 2002).

Steam reforming is a mature technology, which makes it particularly important for the transition to a hydrogen energy economy. Steam reforming is currently operating near its theoretical limit, but hydrogen production is still too expensive compared to the Department of Energy's (DOE) target costs. Additional research and development is needed to move toward the future hydrogen energy economy. Improving reforming efficiencies, developing more durable reforming catalyst, and making advancements in the purification technologies are some of the most essential improvements that must be implemented.

2.3.3. Partial Oxidation

Partial oxidation (POX) is another reforming strategy that is being researched as an option for hydrogen production. During partial oxidation, heavy hydrocarbons, such as diesel, coal, and heavy fuel oils, are reacted with oxygen exothermically at temperatures between 870 and 1400ºC to produce a gaseous mixture containing hydrogen and significant amounts of carbon monoxide. These large amounts of carbon monoxide are due to the limited amounts of oxygen, typically from the air, available to react with the hydrocarbon fuel; which is not stoichiometrically enough to completely oxidize the hydrocarbons to carbon dioxide and water. The partial oxidation reaction is primarily influenced by the oxygen to carbon ratio in the feed. The minimum value for the oxygen to carbon ratio is 1; values lower than 1 generate too much heat and decrease hydrogen concentration (Ahmed et al., 2001).

$$C_nH_{2n} + 0.5nO_2 \rightarrow nCO + nH_2 \qquad (3)$$

Since considerable amounts of carbon monoxide are produced from the first reformation step, it is necessary to introduce the exiting gaseous mixture to water in the form of steam and proceed to a water gas shift (WGS) reactor, the second step in the reformation process, to increase the hydrogen purity and yield in the final product stream. During the water gas shift (WGS) reaction, carbon monoxide is reacted with water to form carbon dioxide and more hydrogen at temperatures around 200°C.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

Partial oxidation reforming is a much faster process and requires a smaller reactor vessel than steam reforming; however, partial oxidation initially produces less hydrogen per unit of fuel than steam reforming of the same fuel.

2.3.4. Auto Thermal Reforming

Among all the reforming strategies, auto thermal reforming is considered to be one of the most effective processes. Auto thermal reforming is a combination of the steam reforming and partial oxidation reforming strategies. During auto thermal reforming vaporized hydrocarbon fuels are reacted with a mixture of reduced amounts of oxygen, from the air, and water in the form of steam to produce a reformate stream containing hydrogen. The ratios of O_2:C and H_2:C are critical for optimal H_2 output and for balancing the energy of the endothermic steam reforming and exothermic partial oxidation reactions, thus auto thermal reforming. This enables the total process to be more energy efficient, since the heat produced from the exothermic partial oxidation reaction can be directly transferred and used by the endothermic steam reforming reaction. This integration enables auto thermal reforming to have better dynamic responses than both steam reforming and partial oxidation.

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + 0.5m\right)H_2 \tag{4}$$

$$C_nH_{2n} + 0.5nO_2 \rightarrow nCO + nH_2 \tag{5}$$

The reactions can take place either simultaneously in one vessel, or they can be separated by a wall in a single vessel with the partial oxidation reaction taking place first (Armor, 1999). The next reforming step requires a water gas shift (WGS) reaction, where the reformate stream is reacted with additional steam to convert the carbon monoxide produced during the first reaction step into carbon dioxide, thus producing more hydrogen.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

The water gas shift (WGS) reaction is essential if the hydrogen from the reformate stream, is to be used in fuel cell applications. The performance of the fuel cell is primarily dependent on the concentrations of hydrogen and carbon monoxide in the reformate stream, that is used to power the fuel cell, thus making the water gas shift reaction a critical process step.

Catalysts are critical factors that affect the efficiency of auto thermal reforming. The catalysts control the extents of the partial oxidation reactions to produce a slightly exothermic process and limit the reactor temperature to allow for smaller system construction (Ahmed et al., 2001).

The advancements in auto thermal reforming technologies have significantly impacted conventional steam reforming plants by decreasing process size, cost, and start up time. Auto thermal reforming is also one of the more marketable reforming technologies, since this reforming strategy is capable of reforming heavy hydrocarbons, such as diesel and gasoline. However, auto thermal reforming is less developed than some of the more conventional reforming technologies and needs much more research and development to become a competitive contender.

2.3.5. Supercritical Methanol Reforming

Supercritical methanol reforming is not a prominent reformation technology yet. However, research has shown various advantages for utilizing this reformation strategy for hydrogen production.

Supercritical reformation utilizes supercritical water instead of steam during hydrocarbon reforming to produce hydrogen at a very high temperature and pressure. Employing supercritical water instead of steam as a reaction medium allows more efficient heat and mass transfer. The advantages of carrying out the reforming reactions in supercritical water over conventional technologies are as follows: the density of supercritical water is much higher than that of steam, which results in a high space-time and the higher values of thermal conductivity and specific heat of supercritical water are beneficial to carry out the endothermic reforming reactions. Furthermore, hydrogen is produced at high pressure, which can be stored directly, thus avoiding the problems associated with its compression. Hydrocarbons are completely soluble in supercritical water, which minimizes the formation of char or slag, which may otherwise lead to catalyst deactivation. (Gadhe et al., 2005).

The major reaction steps involved in the supercritical methanol reforming are as follows: methanol decomposition (6), methanation of carbon monoxide (7), methanation of carbon dioxide (8), and the water gas shift (WGS) reaction (2).

$$CH_3OH \leftrightarrow CO + 2H_2 \tag{6}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{7}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + H_2O \tag{8}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

In addition, the following side reactions, that are responsible for coke formation, can occur during reformation; they are as follows: methane decomposition (9), Boudouard coking (10), and coke gasification (11).

$$CH_4 \leftrightarrow C + 2H_2 \tag{9}$$

$$2CO \leftrightarrow C + CO_2 \tag{10}$$

$$CO + H_2 \leftrightarrow C + H_2O \tag{11}$$

Supercritical methanol reforming has many advantages over the more conventional reformation strategies; nevertheless, more research and development is needed for this reforming strategy to be competitive in future hydrogen production.

2.3.6. Dry Methane Reforming

The dry reforming of methane is not a mature reformation technology either. Dry methane reforming has only been used in combination with steam reforming for commercial applications. The dry methane reforming strategy can be represented by the reaction scheme displayed below. The reforming reaction is shown in reaction (12), followed by the water gas shift (WGS) reaction illustrated by reaction (2). The methane decomposition and Boudouard reactions, expressed by reactions (9) and (13), are both side reactions that can occur during this reforming technology.

$$CH_4 + CO_2 \rightarrow 2CO + H_2 \tag{12}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$CH_4 \rightarrow C + 2H_2 \tag{9}$$

$$CO + CO \leftrightarrow C + CO_2 \tag{13}$$

During dry methane reforming, methane is mixed with carbon dioxide, instead of air and superheated steam in the three primary reformation technologies, and fed to the DMR reactor. Additional steam is fed to the WGS reactor to allow the water gas shift (WGS) reaction to proceed to completion.

Dry methane reforming has the potential to produce synthesis gas at a reduced H_2/CO ratio of (1:1). This type of reformation strategy may also be more beneficial to the environment than other reforming technologies, since both carbon dioxide and methane are greenhouse gases. However, due to the lower H/C ratio, dry methane reforming has a higher potential for carbon formation. Other obstacles are the less favorable thermodynamics that make it more difficult to achieve a sufficiently high conversion of the reactants (Bellona, 2002). Today, extensive research is being conducted to evaluate the kinetics and parameter effects of this reforming technology, primarily to determine if this reforming strategy would be a viable choice for large scale hydrogen production.

2.3.7. Electrolysis

Electrolysis of water has been one of the most investigated hydrogen production processes in the world, thus making it one of the most well-known. However, this process is one of the most energy intensive processing methods. During electrolysis hydrogen is produced by sending an electric current through the water contained in an ionic transfer device to separate water into two components; hydrogen and oxygen. The hydrogen, due to its positive charge, is attracted and collects at the negative anode and the oxygen, due to its negative charge, is attracted and collects at the positive cathode.

Currently the hydrogen that is produced from electrolysis, even though it has a higher purity, is too expensive to produce the quantities needed to serve the energy sector. The high cost associated with this method of hydrogen production is primarily due to the significant amounts of electricity required for this process. Alkaline electrolysis is the most common form and has been used industrially for over 80 years, but is used on a large scale only where cheap electricity is available. (Bellona, 2002). Challenges in performance and cost must be overcome, before these production technologies can be used for large scale hydrogen production.

2.4. Challenges of the Future Hydrogen Economy

2.4.1. Introduction

Along with transportation and storage concerns, the greatest challenge for the future hydrogen energy economy is the cost reduction of hydrogen production. When looking at the production of hydrogen for transportation fuels, the cost must be competitive with conventional fuels and technologies. The cost of hydrogen, regardless of the production technology, must be competitive with gasoline prices. Today's research is directed toward significantly reducing capital equipment, operational, and maintenance costs; in addition, to improving the efficiency of hydrogen production technologies and addressing the environmental emission issues.

2.4.2. Hydrogen Storage

The development of economic and dependable hydrogen storage technologies that meet the cost and performance requirements is vital to achieving a future hydrogen energy economy. Even though hydrogen contains more energy than any other substance on a weight basis, it is the lightest chemical and therefore has an extremely low volumetric energy density. For example, one liter of natural gas contains 5 times more energy than a liter of gaseous hydrogen. (U.S. Department of Energy, 2004) There are three key factors to consider when determining which method of storing hydrogen is most suitable to meet the requirements of the end users, they are: the volume that must be stored, the length of time it must be stored, and the space that is available for storage. The conventional methods of storage are compressed gas cylinders and liquid gas tanks.

Storing hydrogen in high pressure compressed gas cylinders or tanks is currently the cheapest storage method; however, one is faced with the problem of low storage density. Storing hydrogen as a liquid at -253°C will significantly increase the storage density; however, high pressure liquid hydrogen storage vessels are costly and have stricter safety regulations. Also the high pressure liquid storage vessels must be well insulated to minimize evaporation. Today research is being conducted on developing new storage methods and improving the capabilities of the old methods.

Future methods of storage already under development are looking toward storing hydrogen as a solid by absorbing or reacting with metals or chemical compounds. Some of the new developing technologies include: hydrogen absorption using metal hydrides, chemical hydrides, and carbon systems. Advancement in technology is meeting the challenges, with research identifying and addressing today's performance and system issues with hydrogen storage.

2.4.3. Hydrogen Infrastructure

Another major challenge that a future hydrogen energy economy must overcome is the development of an infrastructure to deliver the hydrogen from the production site to the end users. This infrastructure will include all aspects involved in the delivery process, such as: trucks, barges, pipelines, compressors, railway cars, storage facilities, and dispensers. Hydrogen is currently transported by pipeline or by road via cylinders, tube trailers, and cryogenic tankers, with a small amount shipped by rail or barge. (U.S. Department of Energy, 2004). Advancements in hydrogen storage and delivery technology will be needed to meet the requirements for future automotive applications and off board uses.

On board hydrogen storage and dispensing technologies are two of the main branches of research being done today. Breakthroughs in these areas of research are essential for the growth and development of the hydrogen infrastructure.

As of today there is no material available that meets the broad requirements for on board storage of hydrogen. The future of on board storage of gaseous and liquid hydrogen looks grim; however, the storing of hydrogen in chemical compounds offers a much wider range of possibilities for on board hydrogen storage, especially for transportation fuel restrictions. Basic research shows promise of meeting the storage capacity requirements, which is one of the main challenges of on board hydrogen storage, with new innovations of chemical compounds that are capable of storing hydrogen and the enhancement of material performance. Today there are three methods of on board hydrogen storage that are close to commercialization, they are: high pressure gas storage cylinders, cryogenic liquid hydrogen storage tanks, and chemical storage as hydrides.

2.5. Fuel Cell Technology

2.5.1. Introduction

Fuel cell technology has made huge strides in the past couple of years. A fuel cell is conceptually a refuelable battery; however, unlike a normal battery fuel cells are supplied with fuel from an external source. Fuel cells, combine hydrogen and oxygen from the air, to produce electricity; with water being the only byproduct. Also hydrogen fuel cells are silent, have no moving parts, and they do not produce air pollutants. Fuel cells can be used to provide homes and businesses with electricity and heat as well as power vehicles. Using hydrogen in fuel cells is more efficient than combustion, with efficiencies of up to 45%, compared with up to 25% for a dual fuel Internal Combustion Engine (ICE) (U.S. Department of Energy, 2004)

Fuels cells are typically classified either by their main electrolyte, usually alkaline or acidic, or by their feed specifications. Figure 1 illustrates a generic fuel cell diagram (California Energy Commission, 2006). The following basic reactions take place at the electrodes and are represented by reactions (14-16):

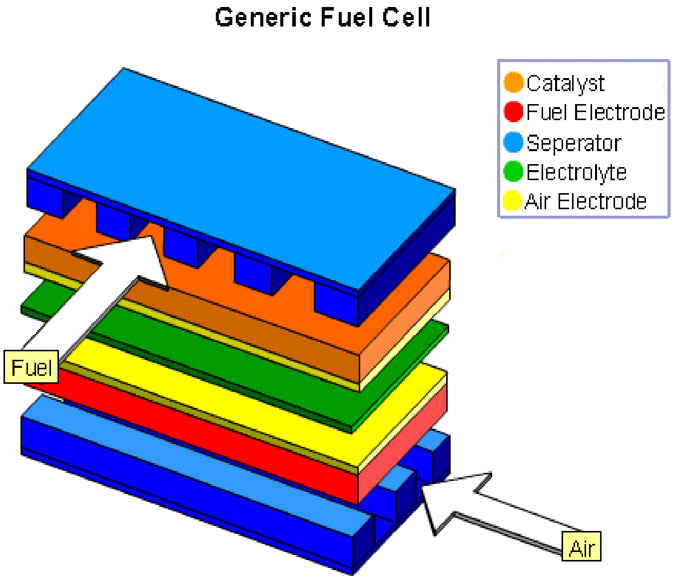


Figure 1. Generic fuel cell schematic

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$ (14)

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (15)

Net: $$2H_2 + O_2 \rightarrow 2H_2O + energy \tag{16}$$

There are three major fuel cell applications, i.e. stationary power, mobile, and portable.

Stationary fuel cell applications include: producing electricity and heat for homes, businesses, and industry. Stationary fuel cell applications will require the development of low cost and reliable grid power and control technology. This new technology will ensure effective operations and high-quality power.

Secondly, mobile applications are where the most extensive research is primarily focused. This application would allow the possible replacement of internal combustion engines with hydrogen fuel cells for transportation applications. As oil prices continue to steadily increase, the driving force for producing hydrogen for transportation fuels and fuel cell powered cars is rapidly increasing. As fuel cell technology develops further this idea comes closer to becoming a reality.

Poor fuel efficiency, depleting oil reservoirs, and irreversible environmental damage are just a few reasons for replacing the century old oil based combustion engine with more advanced and cost efficient hydrogen powered systems. Today, all the major automobile manufactures are developing prototype fuel cell vehicles; some of these prototypes are: Toyota FCHV, GM Hy Wire, and Daimler Chrysler F-Cell.

However, there are many obstacles to overcome to make hydrogen powered vehicles a reality. For mobile applications the fuel processing system must be compact and lightweight to be able to achieve the desirable performance requirements. Another challenge is the removal of contaminates, such as carbon monoxide and hydrogen sulfide.

These contaminates are generated during the reformation of hydrocarbon fuels and can significantly degrade the performance of the fuel cell. Further development in fuel reforming and handling is needed for fuels to eliminate compounds that could poison the fuel cells, and make the application more cost effective.

Finally, portable applications have been divided into to main categories; fuel cell power packs and small portable power generators. Fuel cell power packs will be the future replacement for battery powered applications. Some examples of fuel cells packaged into portable devices are laptop computers, cellular phones, digital cameras, camcorders, and power tools. Portable devices using the power pack technology can store up to 100 watt hours of useable energy. When the device has exhausted the entire amount of stored energy, supplemental energy is available through refueling cartridges.

Small portable power generators usually weigh approximately twenty pounds and can produce somewhere between three and five kilowatts of power for up to two hours. This type of portable fuel cell technology would generally be used for applications, such as: power for campsites, recreational activities, and emergency power systems.

2.5.2. Proton Exchange Membrane Fuel Cells

Proton exchange membrane fuel cell (PEMFC), also referred to as polymer electrolyte fuel cells, have been primarily developed as smaller power generators. The fuel cell utilizes the polymer electrolyte to promote the reaction between hydrogen and oxygen. The PEMFC is the fuel cell technology of choice for most mobile applications, due to its short start up time and low operating temperature of approximately 80°C.

Due to the extreme sensitivity of this type of fuel cell to carbon oxides, platinum based catalysts are required for the PEMFC to achieve the hydrogen purity that is necessary for operating conditions. This is one of the major challenges that must be overcome to make this technology cost effective and economically feasible.

PEMFC are also currently being investigated by the automotive industry, because they are commercially available and the smallest in size (Bernay et al., 2002). Companies which are leading in research and development in these areas are Toshiba, Manhattan Scientifics, Smart Fuel Cells, and Ballard Power Systems.

2.5.3. Molten Carbonate Fuel Cells

Molten carbonate fuel cells (MCFC) initialize the reaction between hydrogen and oxygen to generate electricity and water as a reaction byproduct. The fuel cell has an operating temperature above 500°C, to ensure the electrolyte remains a liquid, thus the system must have an efficient energy source to supply the necessary heat. This high operating temperature can cause corrosion and shorten the lifespan of the fuel cell. Unlike the other types of fuel cell technologies, the MCFC requires a feed of carbon monoxide to its cathode; this allows the fuel cell to be fueled with carbon monoxide and hydrogen, thus eliminating the need for post reformation purification steps. Its current applications are restricted to stationary units for medium-scale power and heat generation due to the size and temperature requirements of the unit (Tomczyk, 2006).

2.5.4. Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFC) utilize ceramic electrolytes and oxidation of carbon monoxide within the cell to generate electricity SOFCs, like MOFCs, have the ability to use carbon monoxide along with hydrogen as fuel to power the cell. SOFCs operate at temperatures above 700°C which will reduce the catalyst cost; however, it can cause corrosion and shorten the lifespan of the fuel cell. These high temperatures increase start up time, but are similar to those used by internal combustion engines (Bernay et al., 2001). This fuel cell technology is best suited for stationary applications mainly due to high temperature operating conditions.

2.6. Test Bed Summary

The Center for Microfibrous Materials Manufacturing (CM^3) at Auburn University has developed a bench scale test bed for investigating running a portable radar system of a Ballard Nexa^{TM} PEM (proton exchange membrane) fuel cell stack by producing high purity hydrogen from reforming jet fuel (JP-8). The PEM fuel cell system consists of both the fuel processing reformer and post reformation clean-up steps and the fuel cell itself. A schematic of the fuel processing test bed is presented in figure 2 and a photo of the actual test bed developed by CM^3 is shown in figure 3.

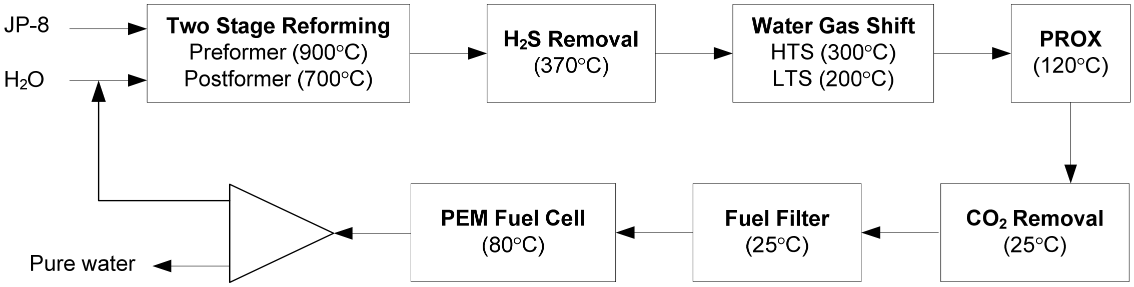


Figure 2. Fuel processing test bed schematic

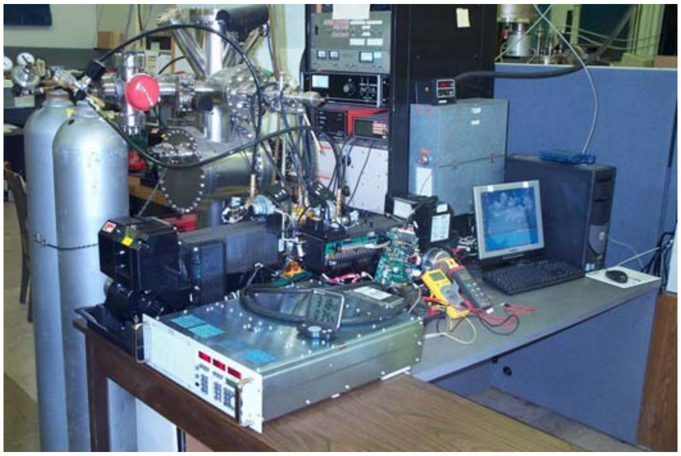


Figure 3. Photograph of fuels processing test bed

The microfibrous catalysts and sorbents inside the test bed enable enhanced heat and mass transfer capabilities by providing high contact efficiency through high surface area to volume ratio. These advanced heat and mass transfer potentials present an opportunity for miniaturization of the processing units compared to conventional catalyst supports, such as packed beds. In figure 4, 500 μm proprietary water gas shift catalysts particles are entrapped in 10-50 μm nickel fibers. Similarly, 150 μm particles of a proprietary precious metal catalyst on alumina support are depicted in figure 5 (Karanjikar et al., 2004; Tatarchuk, 2004.)

Figure 4. WGS catalyst in Nickel fibers

Figure 5. PROX catalyst on Al_2O_3 support

The test bed utilizes steam reformation to produce hydrogen followed by a water gas shift reaction to reduce the CO content from approximately 15% to 1%. The gas chromatograph analysis for the performer and post former effluents are presented in figures 6 and 7.

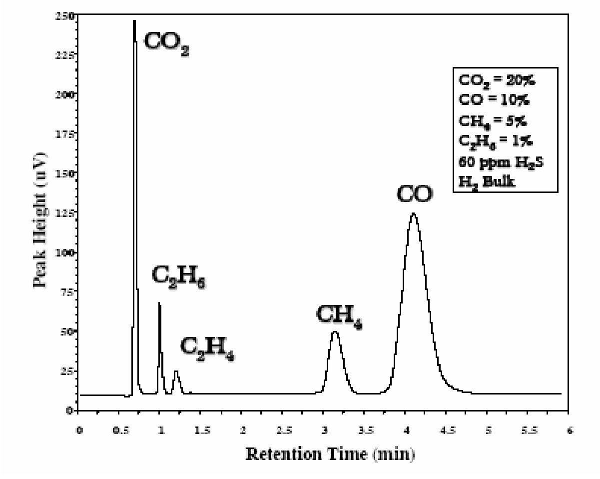


Figure 6. Analysis of preformer effluent by gas chromatography

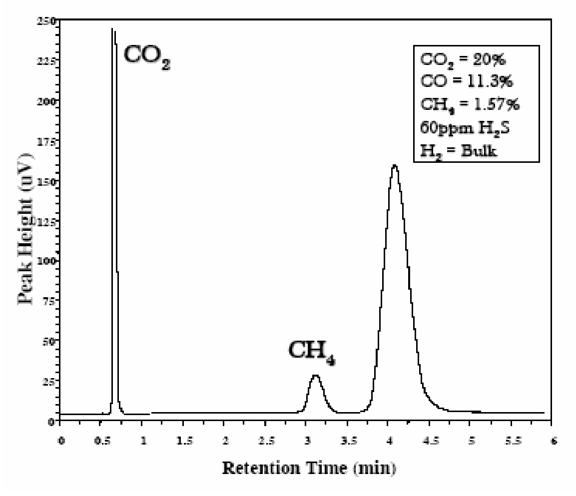


Figure 7. Analysis of postformer effluent by gas chromatography

All processing units after the reformation segment are for hydrogen purification only; by either removing or converting the refomate byproducts. Hydrogen sulfide, which is a catalyst poison, is removed first by a microfibrous entrapped ZnO/SiO_2 catalyst. The hydrogen sulfide content is reduced more than 99% to less than 1 ppm.

The hydrogen sulfide removal is followed by two water gas shift reactors which convert carbon monoxide into carbon dioxide by the addition of additional steam, this reaction is shown below.

$$CO + H_2O \quad \leftrightarrow \quad CO_2 + H_2 \tag{2}$$

The water gas shift reactors reduce the carbon monoxide content from 15% to less than 0.75%. The remaining carbon monoxide is then converted through preferential oxidation (PROX), which decreases the carbon monoxide content to less than 10 ppm. The selectivity of the PROX catalyst ($Pt\text{-}M/AL_2O_3$) towards the oxidation of carbon dioxide is 60%, while the remaining 40% reacts with hydrogen to produce water. The remaining carbon dioxide is then removed by adsorption on a microfibrous entrapped alkaline sorbent. The last unit before the hydrogen rich gas enters the fuel cell is an inline fuel filter, which is a series of microfibrous entrapped sorbents that can remove traces of H_2S, NH_3, CO, and CO_2 (Karanjikar et al., 2004). The hydrogen, once purified, is then fed along with air at atmospheric conditions to the PEM fuel cell. The PEM fuel cell produces electrical power and heat along with pure water as a byproduct.

3. SYSTEM MODELING AND INTEGRATION

3.1. Process Modeling

Simulation models are tools that predict the performance and identify the limitations of processes by evaluating a proposed process flow sheet. Mathematical modeling is the primary basis for all simulation models. Mathematical models are composed of material and energy balances, and are characterized by equations that relate process variables; such as: temperature, composition, pressure, and thermodynamic limitations of the system. These models solve for the unknown process variables at steady state or dynamic conditions. A simulation model is represented by a process flow sheet with multiple units; where each unit signifies a certain process step. Each unit applies computer subroutines, which vary significantly in their degree of complexity due to their particular design specifications, to simulate the various process units. All raw material input streams are depicted by the arrow head pointing toward a process unit and the tail of the arrow is free. The temperature, pressure, component fraction of the flow rate, and the total flow rate must be defined for these input streams. The arrows between the units, where the arrow head and tail are connected to a unit, represent the flow of information between the two individual units. This information is largely dependent upon the specific design constraints. Simulators include the most basic process equipment: heat exchangers, reactors, distillation columns, mixers, splitters, etc (Seider et al., 2004).

A significant benefit of process modeling is the ability to test the sensitivity of the process variables without having to perform numerous, time extensive experiments to generate the same results and conclusions. Optimization of the individual units or the overall process can be evaluated prior to a physical attempt, thus avoiding bottlenecks. Process modeling is also an excellent tool for reviewing design calculations and testing unique equipment features before constructing pilot plant facilities (Cummings, 2005).

3.2. Process Integration

Optimization of all process aspects is a key factor in making the process efficient, environmentally friendly, and economically feasible. Process integration is one of the areas where improvements can be achieved. Integrating heat exchangers and reactors, that is, using streams that need to be cooled to heat other streams may reduce the overall energy consumption. Identifying the process integration potentials and employing them when needed is a proven way to optimize the process.

The tasks of managing the integration of heat exchangers and identifying the optimal allocation of energy are approached through the systematic synthesis of heat exchanger networks (HENs).

The first step in understanding heat integration is to classify the process streams in a systematic way; in heat integration studies, a “cold” stream is a stream that requires heating, while a “hot” stream needs to be cooled (Eden, 2003). Then the minimum external utility load must be identified for the set of process streams. The first method for calculating the minimum values was presented by Hohmann (1971) and further developed by Linnhoff and coworkers (Linnhoff et al., 1982; Linnhoff and Hindmarsh, 1983). El-Halwagi (1997) observes that the streams positioned in an optimal HEN must answer the following questions:

- What is the optimal energy load to be removed or added by each utility?
- How should the process hot and cold streams be matched, i.e. stream pairings?
- What is the optimal system configuration, i.e. how should the heat exchangers be arranged? Do any streams require mixing or splitting?

The thermal pinch analysis is used to depict the areas of opportunity for internal heat exchange between the process streams. Implementing internal heat exchange within the process will significantly reduce the external utility requirements. The individual hot and cold process streams are defined by three steady state parameters; they are the target temperature (T_t), the supply temperature of the stream (T_s), and the heat capacity flow rate (HC). Equation (17) is used to calculate the heat capacity flow rate for streams with no phase change. Equation (18) is formulated to account for the effects on the heat capacity flow rate calculation due to the phase change.

$$HC = m \cdot C_P \tag{17}$$

$$HC = \frac{m \cdot \Delta H}{1K} \tag{18}$$

The pinch point and minimum energy requirements can be determined by either a graphical or algebraic methodology. Aspentech HX-Net^{TM} , the heat integration software used in these research studies, actually utilizes both methods. The graphical methodology is shown in figure 8 (Eden, 2003). Figure 8 depicts the composite curve of the three hot streams with no phase change taking place in the system. The system's cold stream composite curve is constructed through the same methodology. The thermal pinch diagram is achieved when the hot and cold composite curves are graphed together on the same x and y axis. A thermal pinch diagram is shown in figure 9 (Eden, 2003).

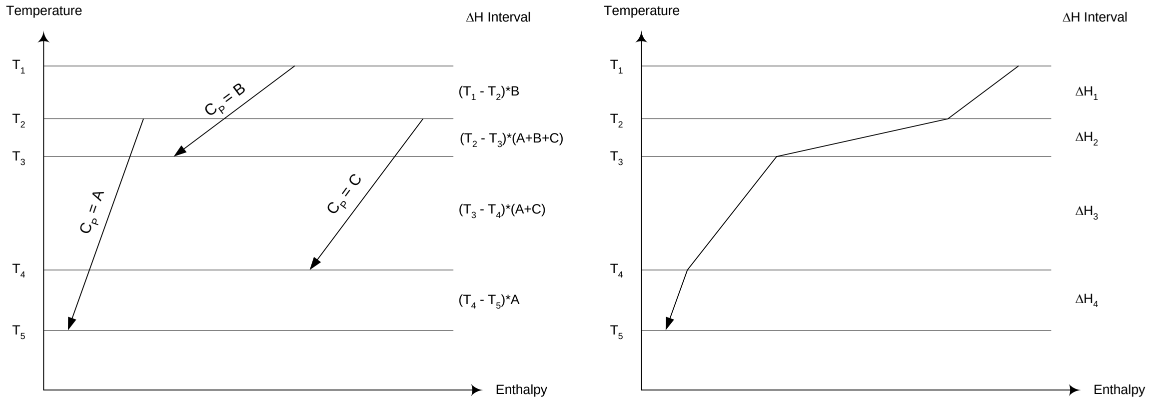


Figure 8. Construction of hot composite curve from three streams.

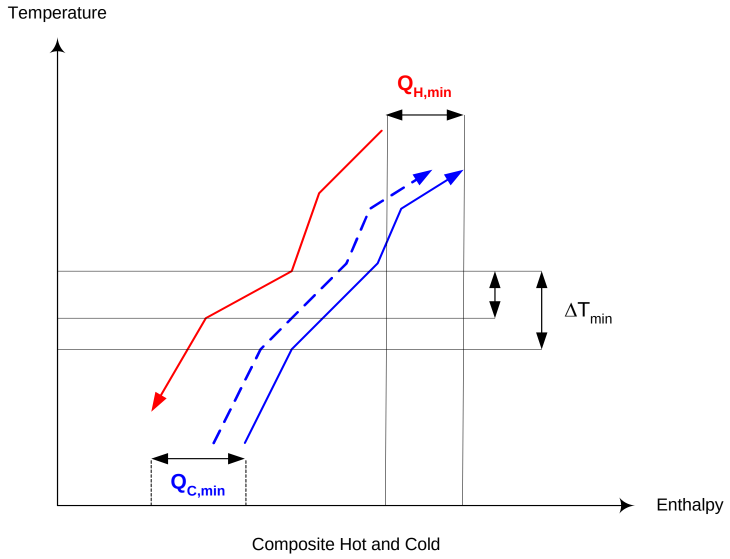


Figure 9. Thermal pinch diagram

The thermal pinch diagram identifies various quantities that represent significant characteristics of the system. The potential for internal heat exchange is represented by the region where the hot and cold composite curves exist over the same enthalpy range. The minimum external heating and cooling utility requirements are illustrated in the regions at the ends of the diagram. The hot and cold composite curves are positioned relative to the minimum allowable temperature driving force ΔT_{min}. Decreasing the minimum allowable temperature driving force (ΔT_{min}) shifts the hot and cold composite curves closer together, thus reducing the external energy that is necessary for the system's requirements and increasing the heat transfer area of the process heat exchangers. When choosing an optimal value for ΔT_{min}, the trade-off between external utility cost and heat exchanger cost must be evaluated.

There are two different graphical techniques which can be used to plot the composite curves when attempting to identify the thermal pinch point. The first step in either technique is to determine the value of ΔT_{min}. One methodology utilizes a shift in the cold composite curve by a distance of ΔT_{min}. Equation (19) represents this shift:

$$T_{HotScale} = T_{ColdScale} + \Delta T_{Min} \tag{19}$$

The hot composite curve will always be a distance of ΔT_{min} from the cold composite curve, when this method is employed. To determine the thermal pinch point, the cold composite curve must be shifted until it touches the hot composite curve; the point at where the curves touch is the thermal pinch point.

The second methodology fixes the location of the hot composite curve and then horizontally shifts the cold composite curve until the shortest distance between the two composite curves is exactly ΔT_{min}. This small region between the two composite curves is referred to as the thermal pinch point. The thermal pinch point signifies a thermodynamic bottleneck of the process. The thermal pinch also divides the energy allocation problem; placing one part of the problem above the pinch and the other part below. The thermal pinch analysis can aid to identify the minimum utility requirements and optimize the energy allocation in the system. Any HEN design may be compared to the energy targets (Eden, 2003). After the pinch point is identified, a HEN may be designed which matches the energy targets, according to three rules stated by Linnhoff et al. (1982):

1. Do not transfer heat across the pinch.

2. Do not use external cooling utilities above the pinch.

3. Do not use external heating utilities below the pinch.

The thermal pinch analysis results in HENs that require the minimum amount of external utilities; however, the proposed designs may not produce the optimal solution in terms of equipment cost. The equipment cost and utility cost must be compared and evaluated to achieve the optimal combination for the system.

4. MODELING PROCEDURE

The process models were developed with Aspen Plus Engineering Suite^{TM}, a commercial process simulation software by Aspen Tech (2004). Large scale and small scale production schemes were simulated for all reformation strategies, to investigate the large and small scale process advantages and disadvantages. The large scale production schemes produce 100,000 Nm^3/hr of hydrogen, while the small scale produces only 1,000 Nm^3/hr. Simulation models were developed for the three primary reformation strategies: steam reforming (SR), partial oxidation (POX), and auto thermal reforming (ATR). To thoroughly investigate the simulation models, two different fuel feeds were utilized to the compare downstream process effects for the large and small scale reformation studies for all three primary reforming strategies. Methane, which was used to represent natural gas, and dodecane, which was employed for the approximation of diesel fuel, were both evaluated as fuel feeds for all three primary reformation strategies. These fuels were also evaluated to supply sufficient heat to the reformers. The compositions of each of these fuels vary according to the source and refinery, so approximations were made. These models were based on simulations done by Seo et al. in 2002, which included the reformer and the WGS reactor. Detailed kinetic data of fuels reformation is rare and difficult to find; because of this, stoichiometric relationships were developed from data produced by Seo et al. (2002).

In addition, simulation models were also developed for two less mature reforming strategies; dry reforming (DR) and supercritical reforming (SC). The supercritical reforming model utilized methanol as the feed fuel; conversely, the dry reforming model employed methane as the feed fuel, which again was used for the approximation of natural gas. These fuels were also evaluated to supply sufficient heat to the reformers through means of combustion. Again, detailed kinetic data of fuels reformation is difficult to locate; given that, stoichiometric relationships were developed for the supercritical reformation models from data generated by Gadhe et al., (2005). The dry reforming models were developed with stoichiometric relationships, which were supported by data published by Shao et al., (2005). Each reformation strategy is explained in considerable detail in the following sections.

5. MODEL SPECIFICATION

5.1. Introduction

A total of sixteen rigorous simulation models have been developed. The first twelve simulation models were developed for steam reforming (SR), partial oxidation (POX), and auto thermal reforming (ATR). Two models were generated for each of the reforming strategies; one on the basis of large scale production and the other on a small scale basis. Methane and dodecane have been reformed by each of the three primary reformation strategies. The following block diagram is the general format of the entire hydrogen production process, including the CO_2 clean-up and the fuel cell implementation for the three primary reformation models. In this work simulation models include the reformation and water gas shift steps only

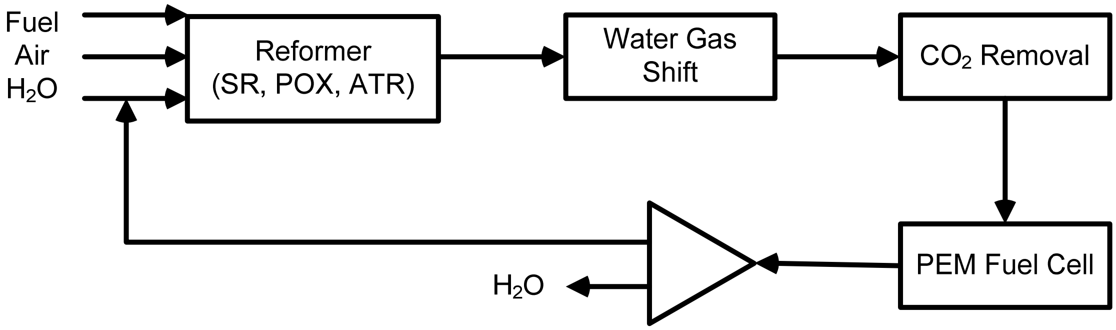


Figure 10. Hydrogen production schematic for the primary reformation strategies

Two of the total sixteen models were developed for supercritical reforming (SC); again, one simulation model on the basis of large scale production and the other on a small scale basis. Methanol was utilized as the reforming fuel for these simulation models. The block diagram below represents the general design of the supercritical reforming models, including the CO_2 removal and the implementation of the fuel cell.

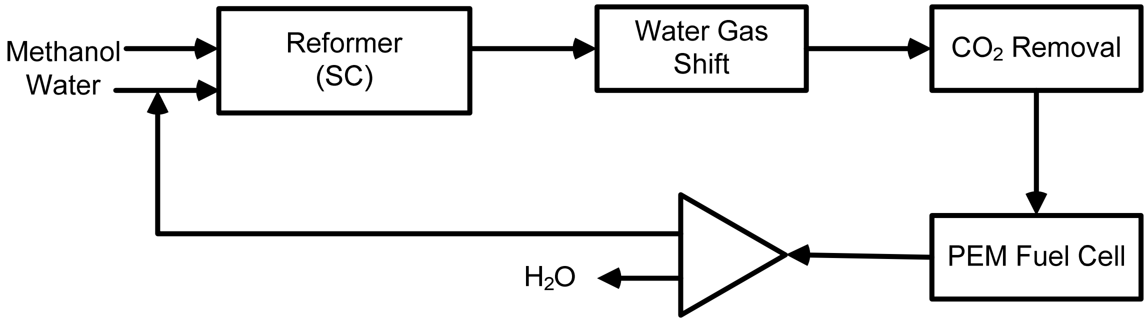


Figure 11. Hydrogen production schematic for Supercritical Methanol Reforming

The final two simulation models were developed for dry reforming (DR). Once more, large and small production basis models were developed. Methane was employed as the reformation fuel for these two models. The following block diagram shows the general format of the dry methane reforming models, including the CO_2 clean up and implementation of the fuel cell.

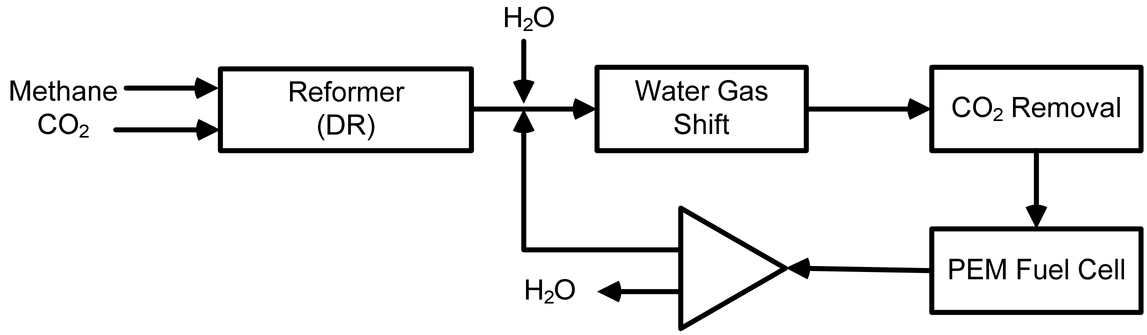


Figure 12. Hydrogen production schematic for Dry Methane Reforming

5.2. Steam Reformation (SR) Models

Steam reforming models were developed for both methane, which was employed to represent natural gas, and dodecane, which was utilized for the approximation for diesel fuel. The steam reforming process (SR) consists of two consecutive steps. First, methane/dodecane is preheated to 400°C then mixed with superheated steam and fed at a C:H_2O ratio of 1:2 to an isothermal SR reactor at 1 atm. The SR reactor is modeled as a conversion reactor and ran at 800ºC and 1 atm. The reactions proceed as follows, depending on the fuel feed: Methane as the primary fuel is represent by reaction (20), while reaction (21) and (22) represents dodecane as the fuel feed. Reduced JP-8, which is discussed in substantial detail in the size constraint analysis section of the thesis, is represented by reactions (23) and (24). Reaction (2) illustrates the WGS clean up for each of the fuels.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \tag{20}$$

$$C_{10}H_{22} + 10H_2O \rightarrow 21H_2 + 10CO \tag{21}$$

$$C_{12}H_{26} + 12H_2O \rightarrow 25H_2 + 12CO \tag{22}$$

$$C_{14}H_{30} + 14H_2O \rightarrow 29H_2 + 14CO \tag{23}$$

$$C_{16}H_{34} + 16H_2O \rightarrow 33H_2 + 16CO \tag{24}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (2)$$

The SR reactor produces synthesis gas, also called syngas, a mixture of primarily hydrogen and carbon monoxide. The syngas is feed to a WGS reactor where the water gas shift (WGS) reaction occurs; reaction (2). The WGS reactor is run isothermally with a feed of steam to carbon monoxide of 2.2:1 (Seo et al., 2002). The WGS reaction takes the carbon monoxide, which is a product from the reforming reaction, and is reacted with additional steam at 200ºC and 1 atm to form hydrogen and carbon dioxide. The water gas shift (WGS) reactor converts 99.1% of carbon monoxide to carbon dioxide. The SR reactions for dodecane have been interpolated from the reactions developed from the reformation of methane in Seo et al. (2002). The extents of the fuel reformation are taken to be 0.991 while the water gas shift (WGS) reaction is 0.214. The hydrogen produced by steam methane reforming still contains impurities; such as, carbon monoxide, carbon dioxide, and hydrogen sulfide. Further purification may be required to remove impurities that can cause complications in some hydrogen applications.

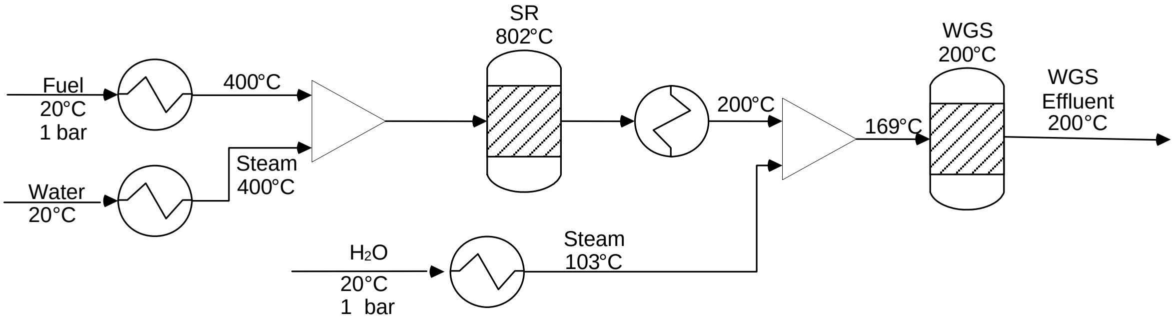


Figure 13. Steam reforming (SR) block diagram

5.3. Partial Oxidation (POX) Models

The partial oxidation models were developed for both methane and dodecane fuel feeds. Partial oxidation reforming consists of a reformation step followed purification step. First, methane/dodecane is mixed with air, which is fed at a C:O_2 ratio of 1.67, and fed to a heater where the feed mixture is preheated to 312ºC and 1 atm. The mixture is then fed to the POX reactor, which is modeled as a conversion reactor operating at 802ºC and 1 atm. The incomplete combustion of the fuel feed produces hydrogen and carbon monoxide. The POX reactor effluent is fed with additional steam to the WGS shift reactor where the water gas shift (WGS) reaction proceeds at 200ºC and 1 atm to produce carbon dioxide and more hydrogen, reaction (2). The WGS reactor is run isothermally with a feed of steam to carbon monoxide of 2.2:1 (Seo et al., 2002). The partial oxidation reforming reaction proceeds as follows, depending on the fuel feed: Reaction (25) represents methane as the fuel feed for the reformation process, while reactions (26) and (27) represent dodecane as the fuel feed. Reactions (28) and (29) represent the reduced JP-8 as the fuel feed. Reaction (2) illustrates the WGS clean up for all the fuels.

$$CH_4 + 0.6O_2 \rightarrow 1.87H_2 + 0.93CO + 0.07CO_2 + 0.13H_2O \qquad (25)$$

$$C_{10}H_{22} + 6O_2 \rightarrow 10.25H_2 + 8.75CO + 1.25CO_2 + 0.75H_2O \qquad (26)$$

$$C_{12}H_{26} + 7.2O_2 \rightarrow 12H_2 + 10.36CO + 1.6CO_2 + 0.89H_2O \qquad (27)$$

$$C_{14}H_{30} + 8.4O_2 \rightarrow 13.97H_2 + 12.23CO + 1.77CO_2 + 1.03H_2O \qquad (28)$$

$$C_{16}H_{34} + 9.6O_2 \rightarrow 15.84H_2 + 13.96CO + 2.04CO_2 + 1.16H_2O \qquad (29)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (2)$$

Since detailed kinetic data of these competing reactions is difficult to acquire, a net reaction was developed based on the experimental data from Seo et al. (2002) and was interpolated for the dodecane simulation reactions. The extent of the reactions is assumed to be 0.9912, calculated from the reactor effluents in Seo's data.

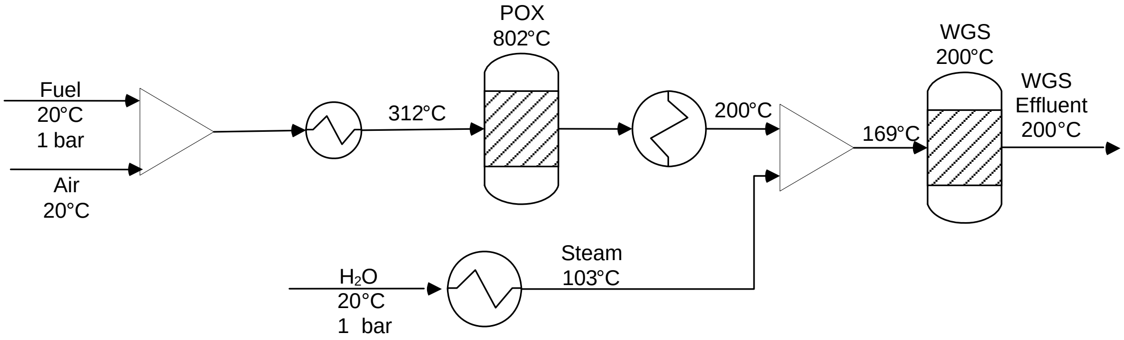


Figure 14. Partial Oxidation (POX) block diagram

5.4. Auto Thermal Reformation (ATR) Models

The auto thermal reformation of hydrocarbon fuels is a combination of the steam reforming and partial oxidation reforming methodologies. The incomplete combustion of some of the feed fuel provides thermal energy for the steam reforming of the remaining fuel. The auto thermal reforming models were simulated for methane and dodecane. Again, natural gas was represented by methane and dodecane was utilized for the approximation of diesel fuel. Methane/dodecane is mixed with air, which is fed at a $C:O_2$ ratio of 1.75, and superheated steam, which is fed at a $C:H_2O$ ratio of 5, then sent to a heater where the mixture is preheated at 400ºC and 1 atm. The ATR reactor is modeled as a conversion reactor and operates at 788ºC and 1 atm. The reactions proceed as follows, depending on the fuel feed: Methane is represented in reaction (30) as the fuel feed, while reactions (31) and (32) represent dodecane as the feed fuel. Reactions (33) and (34) represent reduced JP-8 as the feed fuel. Reaction (2) illustrates the WGS clean up for each of the feed fuels.

$$0.35CH_4 + 0.20O_2 \rightarrow 0.70H_2 + 0.31CO + 0.04CO_2 \tag{30}$$

$$C_{10}H_{22} + 5.45O_2 \rightarrow 11H_2 + 9.10CO + 0.90CO_2 \tag{31}$$

$$C_{12}H_{26} + 6.54O_2 \rightarrow 13H_2 + 10.92CO + 1.08CO_2 \tag{32}$$

$$C_{14}H_{30} + 7.63O_2 \rightarrow 15H_2 + 12.74CO + 1.26CO_2 \tag{33}$$

$$C_{16}H_{34} + 8.72O_2 \rightarrow 17H_2 + 14.56CO + 1.44CO_2 \tag{34}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{35}$$

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{36}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{2}$$

While steam is fed to the reformer, there is a net generation of steam in the reformer from the reaction of hydrogen with oxygen; this generation corresponds to equation (35). The ATR reactor effluent is then fed with additional steam to the WGS reactor. The WGS reactor is run isothermally with a feed of steam to carbon monoxide of 2.2:1 (Seo et al., 2002). The water gas shift (WGS) reaction proceeds at 200ºC and 1 atm, where more hydrogen is produced with carbon dioxide, reaction (2). Once again, detailed kinetics are not available for this reformation strategy, net reactions were developed for the fuel components to represent the reformation combinations from experimental data in Seo et al. (2002). The extent of the net fuel reformation reactions is 0.9912, while the extent of the water production is 1.0 because all the oxygen is consumed in the reformer. A schematic for the ATR models is shown below in figure 15.

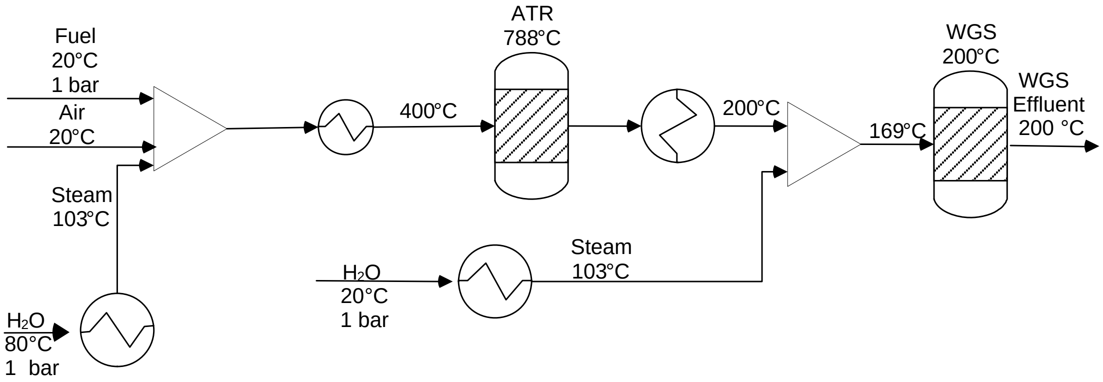


Figure 15. Auto Thermal reformation (ATR) block diagram

5.5. Supercritical (SC) Methanol Reformation Models

The supercritical methanol reforming simulation models were developed for both large and small scale hydrogen production. First, the methanol and water are heated to 600ºC and compressed to 276 bar. Then the feed mixture is sent to the SC reactor, which operates under these same conditions. The SC reactor is modeled after a yield reactor. The molar yields for methane, carbon dioxide, carbon monoxide, hydrogen, and water are as follows: $9.65 \cdot 10^{-5}$, $2.83 \cdot 10^{-3}$, $2.89 \cdot 10^{-4}$, $8.97 \cdot 10^{-3}$, and $4.73 \cdot 10^{-2}$, respectively. Detailed kinetic data for fuel reformation is difficult to find; therefore, the simulation models were developed based on yield data published by Gupta et al., (2005). The reactor effluent is first cooled and then feed to the WGS reactor at isothermal operating conditions of 200ºC and 1 atm, where the water gas shift (WGS) reaction proceeds. The water gas shift (WGS) reaction converts 99.1% of the carbon monoxide to carbon dioxide. The water gas shift (WGS) reaction is illustrated by reaction (2).

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (2)$$

Supercritical methanol reforming demonstrates some advantages such as enhanced heat and mass transfer, higher operating pressure, and hydrocarbon solubility in supercritical water. However, more research and development must be conducted to evaluate this reformation technology as another choice for long term hydrogen production.

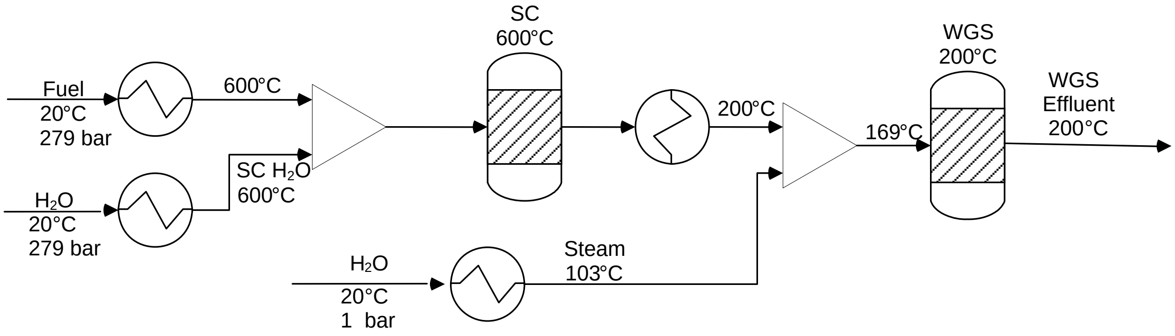


Figure 16. Supercritical (SC) Methanol reformation block diagram

5.6. Dry (DR) Methane Reformation Models

A large and small scale simulation model was developed for the dry methane reforming strategy. Methane and carbon dioxide is mixed and sent to a heater where the mixture feed was preheated and then sent to the DMR reactor, which operates at 850ºC and 5 atm using cobalt-tungsten carbide catalyst. The DMR reactor was modeled as a conversion reactor. Reactions (37) and (38), illustrate the reforming reaction and the methane decomposition side reaction which occur within the DMR reactor. The reforming reaction is defined by a carbon dioxide fractional conversion of 0.78; conversely, the methane decomposition reaction is defined by a methane fractional conversion of 0.18.

$$CH_4 + CO_2 \rightarrow 2CO + H_2 \tag{37}$$

$$CH_4 \rightarrow C + 2H_2 \tag{38}$$

The reactor effluent is cooled, then mixed with steam and sent to the WSG reactor, where the water gas shift (WGS) reaction proceeds at isothermal conditions of 200ºC and 1 atm. The water gas shift (WGS) reaction converts 99.1% of carbon monoxide to carbon dioxide. The water gas shift reaction is illustrated below.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

Since this reformation strategy is not as mature and detailed kinetic data is difficult to locate, these reformation models were simulated uses the data provided by Shao et al., (2005).

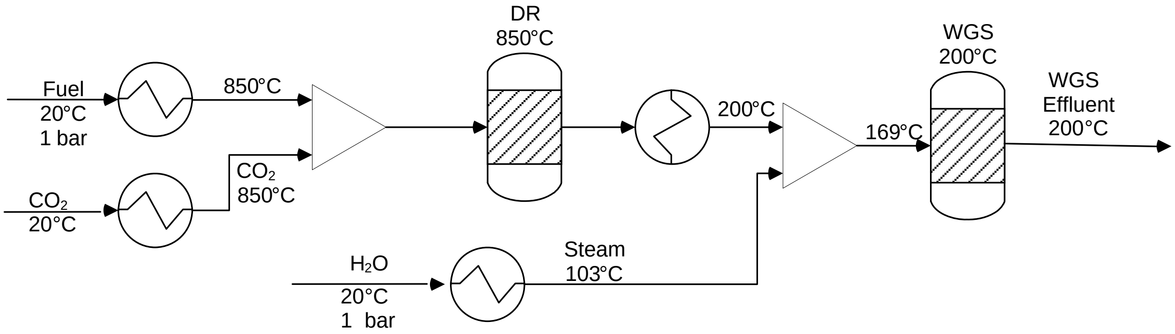
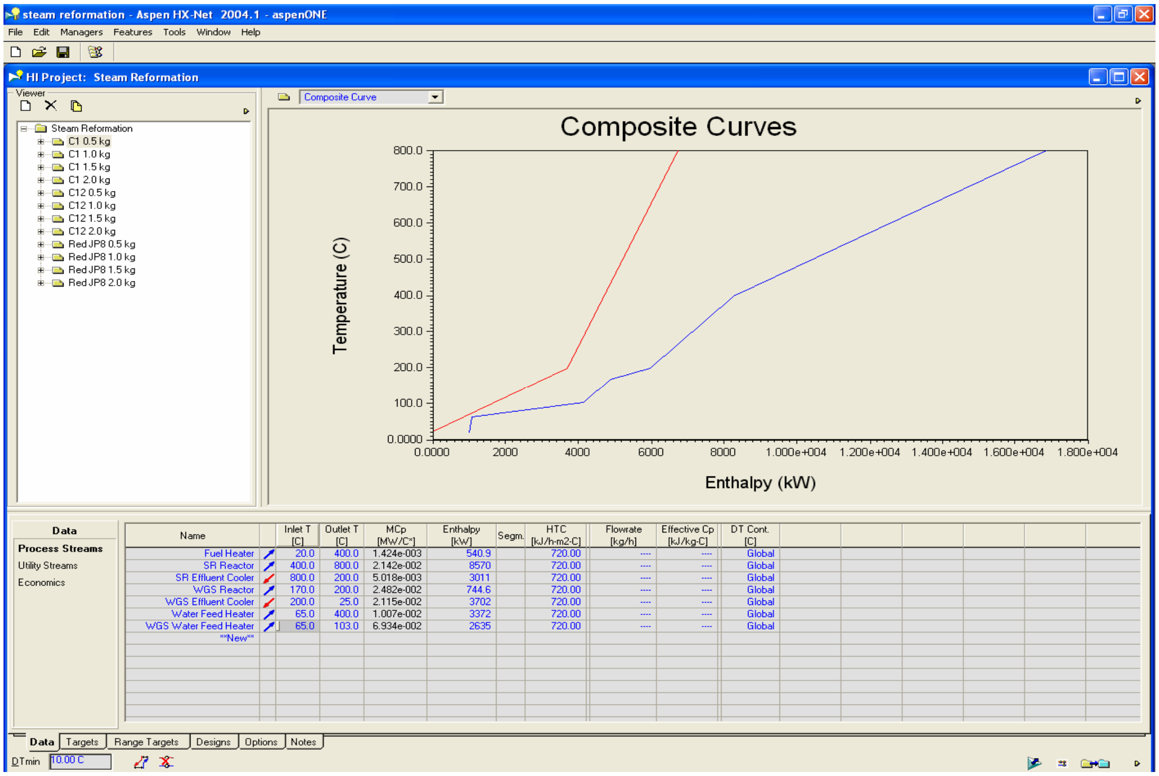


Figure 17. Dry (DR) Methane reformation block diagram

6. HEAT INTEGRATION PROCEDURE

The evaluation of hydrogen production processes would not be adequately complete without identifying and implementing the possible opportunities for thermal integration. Given that hydrogen is already at an uncompetitive cost level compared to fossil fuels, assessments of the heating and cooling utility requirements and potential opportunities to reduce their usage is imperative. Integration of the system's heaters and coolers should be completed for all the reformation strategies, to reduce the overall process energy consumption and to evaluate how the energy demands affect the total capital cost of the process. Temperature difference values and duties were extracted from each heat exchanger and reactor in the system to determine heating and cooling utility requirements of the processes. The temperature difference values and duties of the various streams were then entered into Aspen Tech HX-Net^{TM} , a computer software program that calculates minimum heating and cooling targets and develops heat exchanger network designs for process optimization through the integration of hot and cold streams. A screenshot of the HX-NET stream data input page is shown in figure 18 below.



Name		Inlet T [C]	Outlet T [C]	MCp [MW/C*]	Enthalpy [kW]	Segm.	HTC [kJ/h-m2-C]	Flowrate [kg/h]	Effective Cp [kJ/kg-C]	DT Cont. [C]
Fuel Heater	↗	20.0	400.0	1.424e-003	540.9		720.00	----	----	Global
SR Reactor	↗	400.0	800.0	2.142e-002	8570		720.00	----	----	Global
SR Effluent Cooler	↙	800.0	200.0	5.018e-003	3011		720.00	----	----	Global
WGS Reactor	↗	170.0	200.0	2.482e-002	744.6		720.00	----	----	Global
WGS Effluent Cooler	↙	200.0	25.0	2.115e-002	3702		720.00	----	----	Global
Water Feed Heater	↗	65.0	400.0	1.007e-002	3372		720.00	----	----	Global
WGS Water Feed Heater	↗	65.0	103.0	6.934e-002	2635		720.00	----	----	Global
New										

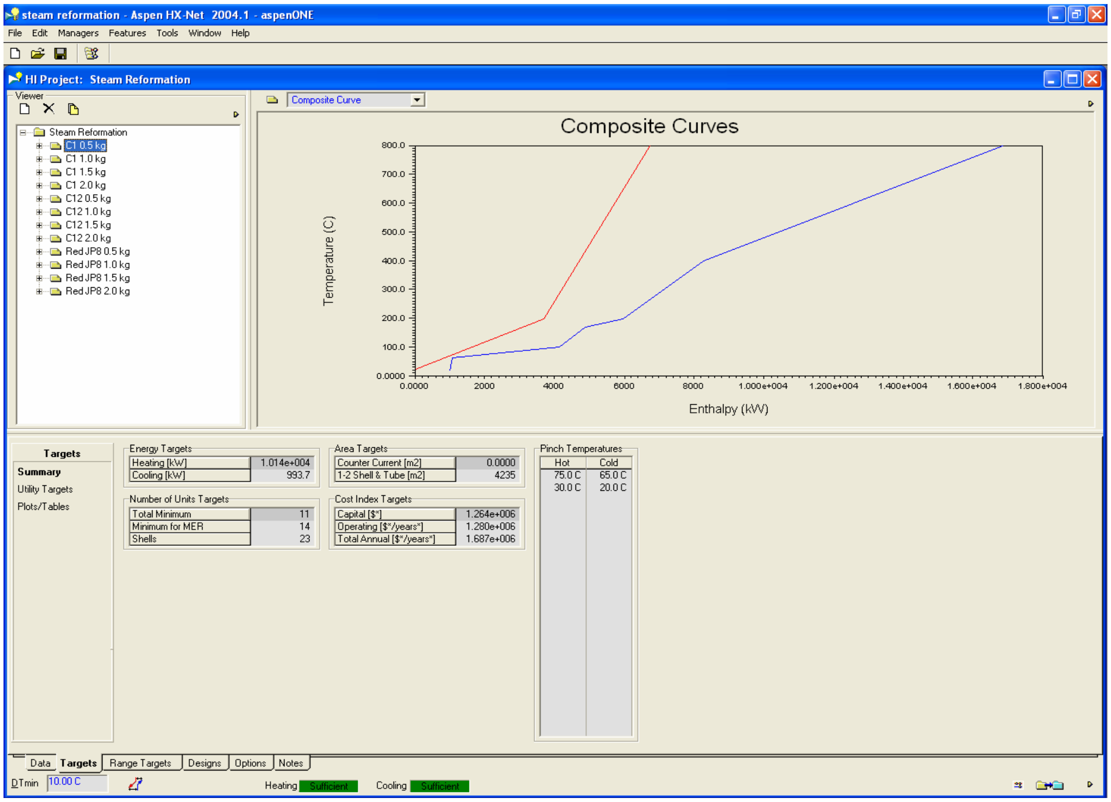
DTmin 10.00 C

Figure 18. Stream data input form in Aspentech HX-Net

The upper section of the screen depicts a thermal pinch diagram, which is developed from the input temperature difference and enthalpy data collected from each heat exchanger and reactor in the system. The pinch diagram is a graphical representation of the how the heating and cooling demands of the processes can be optimized; such as, the excess heating can be utilized to heat cold streams, while the excess cooling can be employed to cool hot streams.

The lower section of the screen allows the user to input a steam identification name, temperature difference values of the heat exchangers and reactors, and the enthalpy change of each stream during heating or cooling. The HX-Net software automatically generates the heat capacity of each stream on the basis of the supplied temperature difference data and enthalpy specifications.

The HX-Net software generates candidate heat exchanger network designs based on minimizing the total annualized cost of the utility requirements and process equipment size. The software also allows the user to choose the option to match a specific stream with only the external utility streams; this option is achieved by forbidding all other internal stream matching. Two heat exchanger networks were generated for each of the various reformation strategies, large and small scale production schemes. One heat exchanger network design was developed allowing internal stream matching; therefore, permitting streams to be matched with both reactor streams and external utility streams. The other designed network prohibits internal stream matching with the reactor streams; so, streams were only allowed to be matched with the external utility streams. These two heat exchanger networks were developed to evaluate the total capital cost of process when internal stream matching is allowed and when it is not. Figure 19 depicts a screenshot of an example heat exchanger network design generated by Aspentech HX-Net.



Energy Targets

Heating [kW]	1.014e+004
Cooling [kW]	993.7

Area Targets

Counter Current [m2]	0.0000
1-2 Shell & Tube [m2]	4235

Number of Units Targets

Total Minimum	11
Minimum for MER	14
Shells	23

Cost Index Targets

Capital [$*]	1.264e+006
Operating [$*/years*]	1.280e+006
Total Annual [$*/years*]	1.687e+006

Pinch Temperatures

Hot	Cold
75.0 C	65.0 C
30.0 C	20.0 C

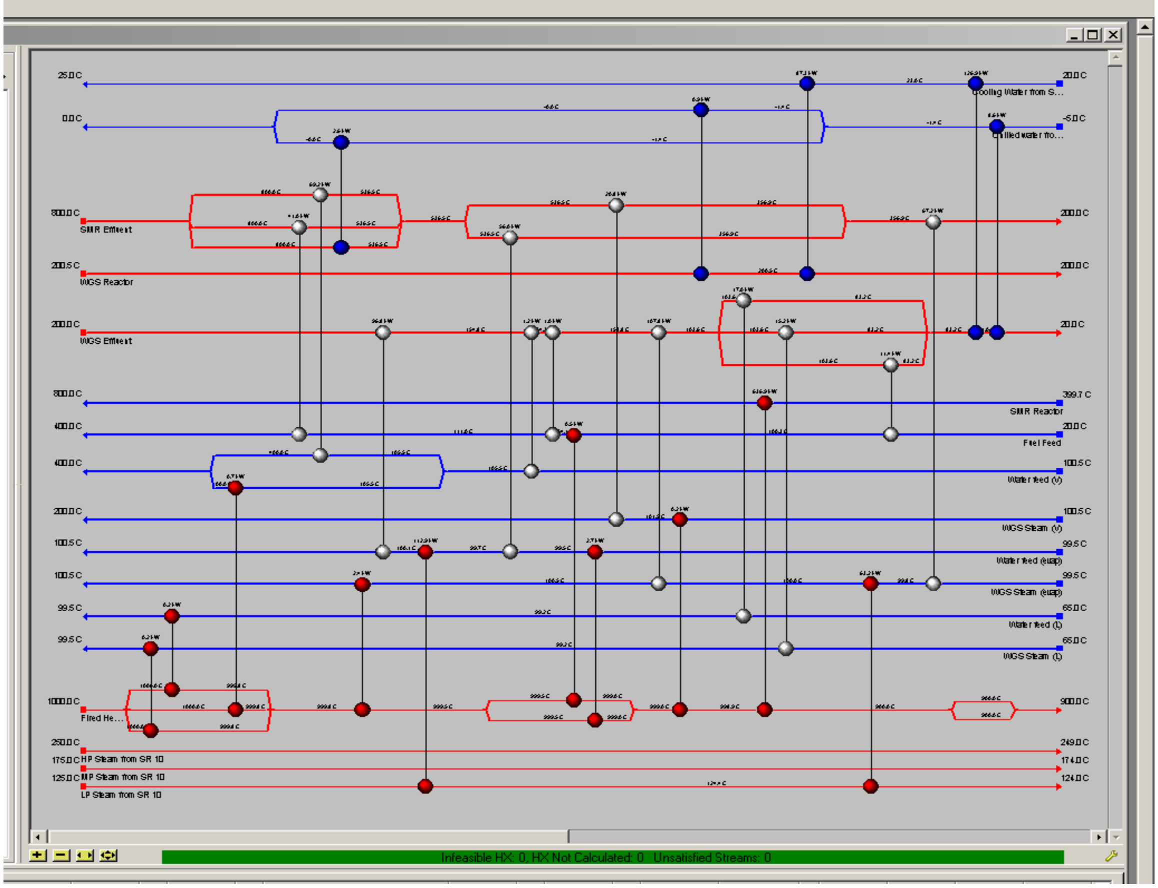
DTmin 10.00 C

Heating Sufficient

Cooling Sufficient

Figure 19. Pinch analysis summary from Aspentech HX-Net

Once the stream data has been completely specified, HX-Net calculates the minimum heating and cooling requirements of the system on the basis of conventional pinch analysis methodologies. The software also calculates the total capital cost, the theoretical minimum area of the shell tube heat exchangers necessary to fulfill the minimum utility requirements, and the minimum number of heat exchangers necessary to achieve the target. Figure 19 illustrates a screenshot of the pinch analysis summary and the targets of the heating and cooling energies, total capital cost, minimum area, and minimum number of necessary heat exchanger units. The software also supplies information on the pinch temperature of the process and the size of the thermal loads the utilities are required to carry. The total capital cost was the primary target that was utilized for the comparison of the multiple reformation strategies and variation in the fuel complexity.



Infeasible HX: 0, HX Not Calculated: 0 Unsatisfied Streams: 0

Figure 20. Example heat exchanger network generated in Aspentech HX-Net

7. ECONOMIC ANALYSIS

The economic analysis for each of the reformation strategies was evaluated using Aspen Tech Icarus^{TM} Process Evaluator; which is a computer software program that calculates economic values, such as: the total project capital cost, total operating cost, total utility cost, total raw material cost, and the total product sales. The raw material and product flow rates along with the current chemical cost were entered into Icarus to allow the software to compute up to date raw material cost and product sales for each year. The current costs were inferred from *Chemical Market Reporter* and are as follows: 0.004 $/mol for methane, which represents natural gas; 0.16 $/mol for dodecane, which signifies diesel; 0.00000828 $/mol for water; 0.0085 $/mol for methanol; and 0.000783 $/mol for carbon dioxide.

The minimum cost heat exchanger network areas and number of shells per each heat exchanger unit were extracted from HX-Net and also imported into Icarus to accurately calculate the cost of each heat exchanger process unit. The cost analysis calculations for reactors are complex, so the reactor costs were calculated separately by combination of heat exchanger cost estimation methods from Peters et al (2003), Lang factors provided by contacts in the chemical industry, and graphical linear relationships. Then the reactor costs were independently specified in Icarus. First, the volumetric reactor feed rates were extracted from the reformation models and a residence time of seven seconds was assumed to calculate the reactor volume utilizing equation (39). Next the tube volume was calculated for a reactor outer diameter of two inches and length of twenty feet. Dividing the reactor volume by the tube volume will yield the surface area of the tube; equation (40). The total area is then calculated by multiplying the number of tubes by the area of the tube; equation (41).

$$V_R = \dot{V} \cdot \tau \tag{39}$$

$$A_{TUBE} = \frac{V_R}{V_T} \tag{40}$$

$$A_{TOTAL} = N_{TUBES} \cdot A_{TUBE} \tag{41}$$

After the reactor areas were calculated, a linear relationship was developed between the reactor costs and the areas. The linear relationship was utilized to calculate the cost of the reformers, WGS, and combustion reactors. The linear relationship between the reactor cost and area is illustrated in figure 21.

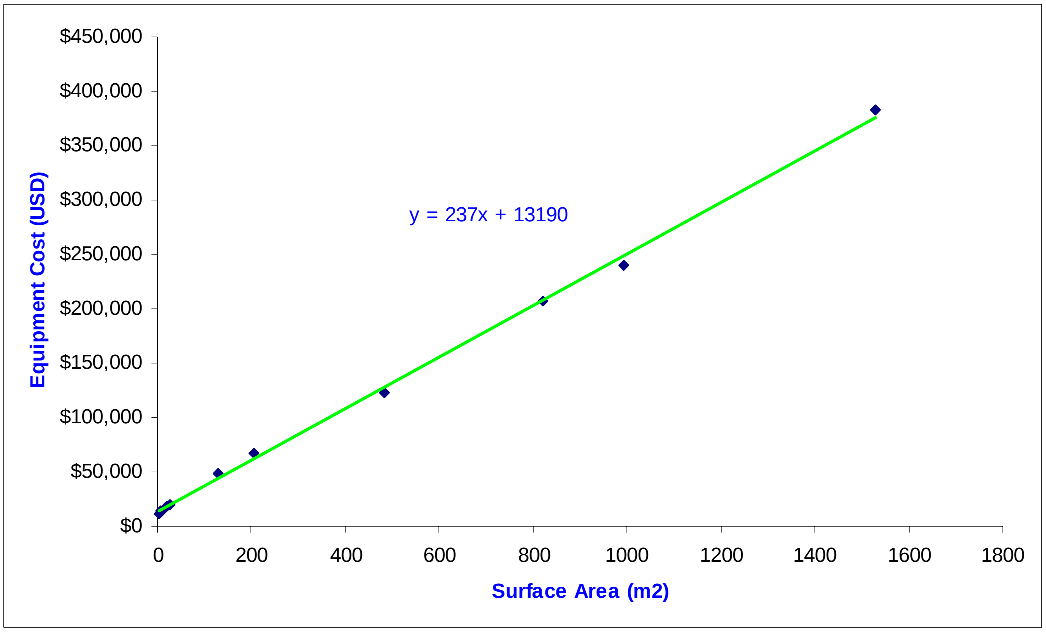
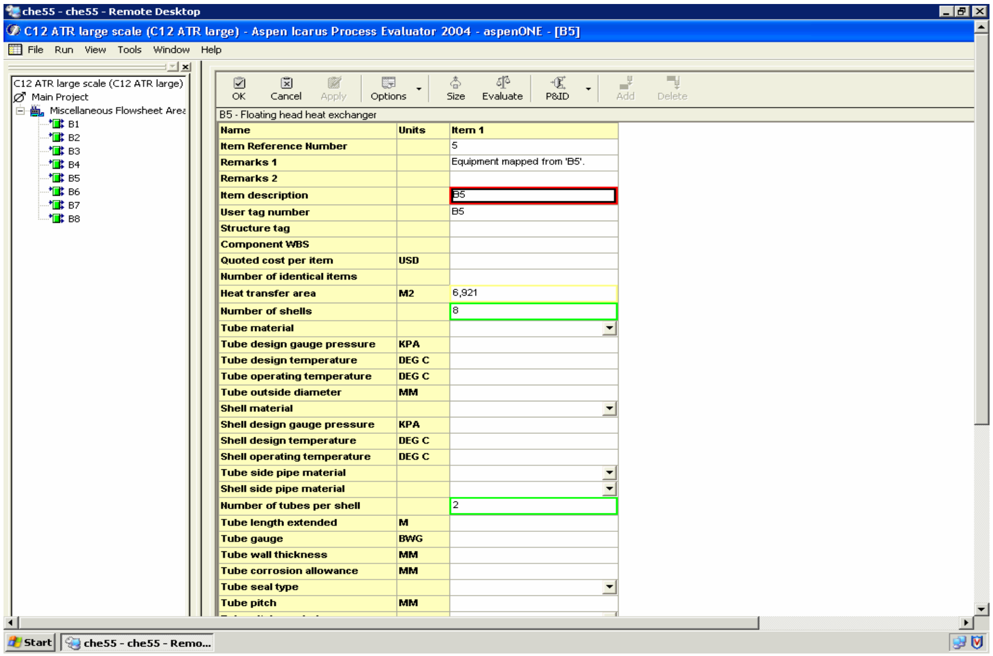


Figure 21. Linear relationship between the reactor cost and the area.

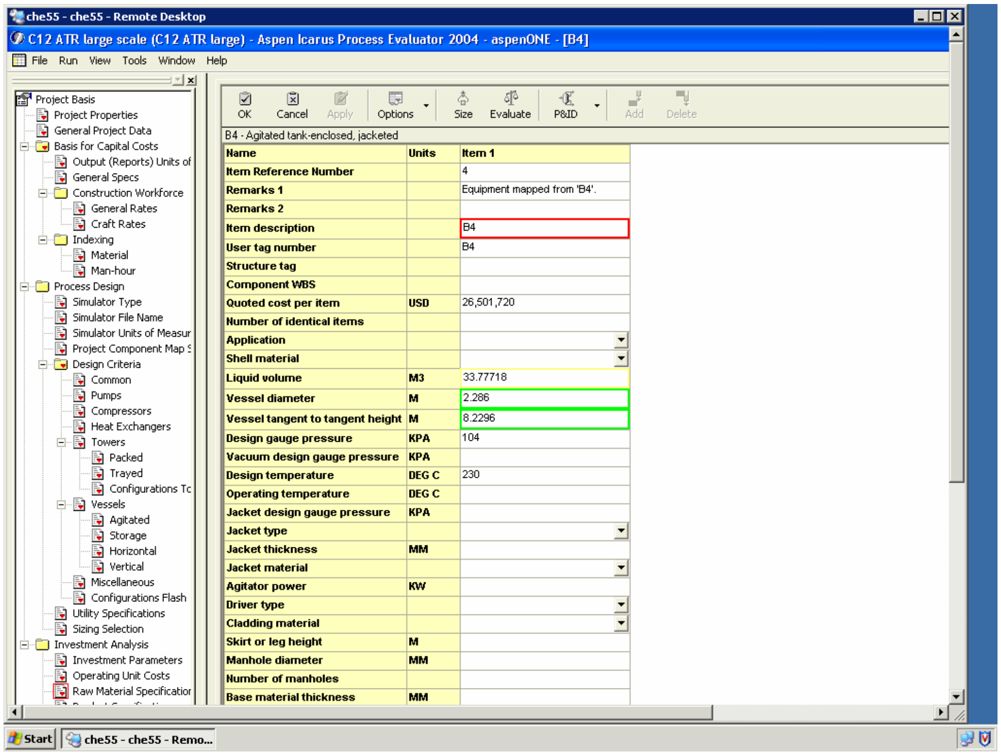
The independently calculated costs are then entered into Icarus for each of the reformers, WGS, and combustion reactors. A screenshot of the Icarus equipment cost analysis data input pages for heat exchangers and reactors are shown in figures 22 and 23 below.



B5 - Floating head heat exchanger

Name	Units	Item 1
Item Reference Number		5
Remarks 1		Equipment mapped from 'B5'.
Remarks 2		
Item description		B5
User tag number		B5
Structure tag		
Component WBS		
Quoted cost per item	USD	
Number of identical items		
Heat transfer area	M2	6,921
Number of shells		8
Tube material		
Tube design gauge pressure	KPA	
Tube design temperature	DEG C	
Tube operating temperature	DEG C	
Tube outside diameter	MM	
Shell material		
Shell design gauge pressure	KPA	
Shell design temperature	DEG C	
Shell operating temperature	DEG C	
Tube side pipe material		
Shell side pipe material		
Number of tubes per shell		2
Tube length extended	M	
Tube gauge	BWG	
Tube wall thickness	MM	
Tube corrosion allowance	MM	
Tube seal type		
Tube pitch	MM	

Figure 22. Heat exchanger cost analysis data input page in Aspentech Icarus

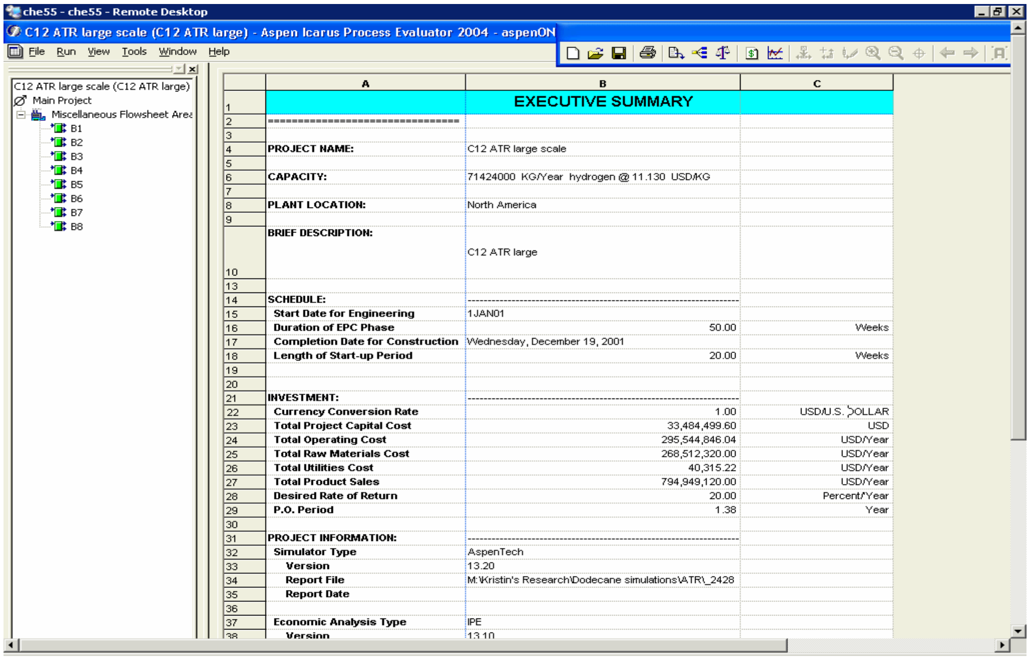


B4 - Agitated tank-enclosed, jacketed

Name	Units	Item 1
Item Reference Number		4
Remarks 1		Equipment mapped from 'B4'.
Remarks 2		
Item description		B4
User tag number		B4
Structure tag		
Component WBS		
Quoted cost per item	USD	26,501,720
Number of identical items		
Application		
Shell material		
Liquid volume	M3	33.77718
Vessel diameter	M	2.286
Vessel tangent to tangent height	M	8.2296
Design gauge pressure	KPA	104
Vacuum design gauge pressure	KPA	
Design temperature	DEG C	230
Operating temperature	DEG C	
Jacket design gauge pressure	KPA	
Jacket type		
Jacket thickness	MM	
Jacket material		
Agitator power	KW	
Driver type		
Cladding material		
Skirt or leg height	M	
Manhole diameter	MM	
Number of manholes		
Base material thickness	MM	

Figure 23. Reactor cost analysis data input page in Aspentech Icarus

Once the raw material and product flow rates along with the current chemical and reactor costs are entered into Icarus, the computer software is now capable of generating economic data: such as, total production capital cost, total operating cost, total utility cost, total raw material cost, and total product sales. The screenshot below illustrates the economic results generated by Icarus.

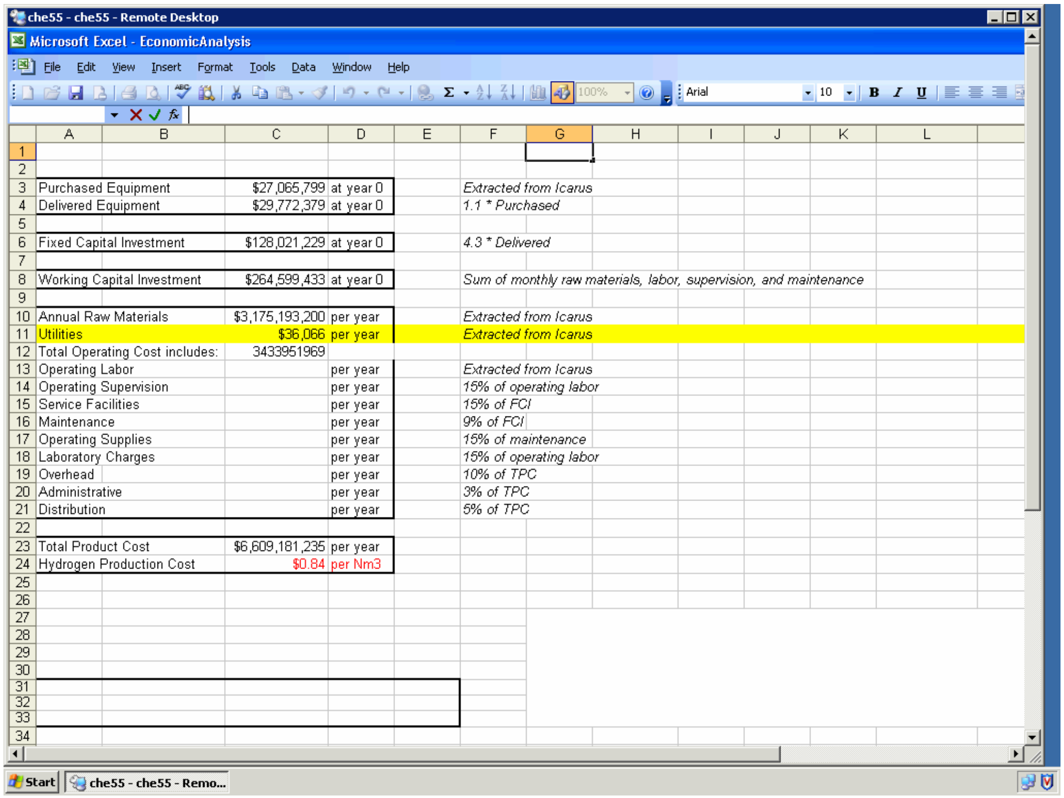


	A	B	C
1		EXECUTIVE SUMMARY	
2	=================================		
3			
4	**PROJECT NAME:**	C12 ATR large scale	
5			
6	**CAPACITY:**	71424000 KG/Year hydrogen @ 11.130 USD/KG	
7			
8	**PLANT LOCATION:**	North America	
9			
10	**BRIEF DESCRIPTION:**	C12 ATR large	
13			
14	**SCHEDULE:**	--	
15	**Start Date for Engineering**	1JAN01	
16	**Duration of EPC Phase**	50.00	Weeks
17	**Completion Date for Construction**	Wednesday, December 19, 2001	
18	**Length of Start-up Period**	20.00	Weeks
19			
20			
21	**INVESTMENT:**	--	
22	**Currency Conversion Rate**	1.00	USD/U.S. DOLLAR
23	**Total Project Capital Cost**	33,484,499.60	USD
24	**Total Operating Cost**	295,544,846.04	USD/Year
25	**Total Raw Materials Cost**	268,512,320.00	USD/Year
26	**Total Utilities Cost**	40,315.22	USD/Year
27	**Total Product Sales**	794,949,120.00	USD/Year
28	**Desired Rate of Return**	20.00	Percent/Year
29	**P.O. Period**	1.38	Year
30			
31	**PROJECT INFORMATION:**	--	
32	**Simulator Type**	AspenTech	
33	**Version**	13.20	
34	**Report File**	M:\Kristin's Research\Dodecane simulations\ATR_2428	
35	**Report Date**		
36			
37	**Economic Analysis Type**	IPE	
38	**Version**	13.10	

Figure 24. Results from the Icarus economic analysis

Further economic analyses were completed by extracting the delivered equipment cost, raw material cost, total operating cost and the total utility cost from Icarus and utilizing economic cost relationships provided by Peters et al (2003). This extracted data and the Microsoft Excel goal seek tool were utilized to calculate the hydrogen production cost in \$/Nm^3 .

A screenshot of the excel spreadsheet economic calculations and formulas in shown in figure 25.



	A	B	C	D	E	F
1						
2						
3	Purchased Equipment		$27,065,799	at year 0		*Extracted from Icarus*
4	Delivered Equipment		$29,772,379	at year 0		*1.1 * Purchased*
5						
6	Fixed Capital Investment		$128,021,229	at year 0		*4.3 * Delivered*
7						
8	Working Capital Investment		$264,599,433	at year 0		*Sum of monthly raw materials, labor, supervision, and maintenance*
9						
10	Annual Raw Materials		$3,175,193,200	per year		*Extracted from Icarus*
11	Utilities		$36,066	per year		*Extracted from Icarus*
12	Total Operating Cost includes:		3433951969			
13	Operating Labor			per year		*Extracted from Icarus*
14	Operating Supervision			per year		*15% of operating labor*
15	Service Facilities			per year		*15% of FCI*
16	Maintenance			per year		*9% of FCI*
17	Operating Supplies			per year		*15% of maintenance*
18	Laboratory Charges			per year		*15% of operating labor*
19	Overhead			per year		*10% of TPC*
20	Administrative			per year		*3% of TPC*
21	Distribution			per year		*5% of TPC*
22						
23	Total Product Cost		$6,609,181,235	per year		
24	Hydrogen Production Cost		$0.84	per Nm3		

Figure 25. Microsoft Excel spreadsheet economic calculations and formulas.

Figure 25 illustrates the economic relationships employed to calculate the fixed capital investment, working capital investment, total product cost, and hydrogen production cost.

The fixed capital investment represents the capital necessary for the installed process equipment with all components that are needed for complete process operation. The working capital investment entails the total amount of money invested in raw materials and supplies carried in stock, the finished products in stock and semi finished products in the process of being manufactured, the accounts receivable, the cash kept on hand for monthly payment of operating expenses, accounts payable, and taxes payable. The total product cost consists of total plant operating cost, selling the products, recovering the capital investment, and contributing to corporate functions. The economic analysis results for each of the reformation strategies are discussed in significant detail in the following chapter.

8. ANALYSIS OF LARGE AND SMALL SCALE HYDROGEN PRODUCTION

Detailed data reports for both large and small scale production and economic cost analysis were generated for the fuel models for steam reformation (SR), partial oxidation (POX), auto thermal reformation (ATR), supercritical methanol reformation (SC), and dry methane reformation (DR). The reports are included on a CD in Appendix A. Large and small scale hydrogen production processes were investigated with an hourly hydrogen production rate of 1240 mols/hr for large scale production and 12.40 mols/hr for small scale. Duties for heat exchangers and reactors were extracted from the units, as well as the compositions of the reformer and the water gas shift (WGS) effluents. Minimum heating and cooling requirements along with the minimum required heat exchanger areas were extracted from HX-Net. A summary of the representative integration potential results for both large and small scale production is presented in Tables 1 and 2. It should be noted that two scenarios were investigated for each reformation process. The first scenario allowed the reactors to be included in the heat exchanger network; while, the second scenario used only external utilities to heat or cool the reactors. Insights into the preferred reformation strategy based on cost savings from integration may be seen from the comparison of minimum utility demands of each strategy.

Methane (CH_4)	**Heating Utilities (kW)**		**Cooling Utilities (kW)**	
	w/o Reactors	**w/ Reactors**	**w/o Reactors**	**w/ Reactors**
POX	16120 (-73%)	2836 (-95%)	13870 (-76%)	578 (-99%)
SR	127600 (-19%)	117800 (-25%)	10180 (-74%)	394 (-99%)
ATR	27040 (-61%)	11990 (-83%)	15850 (-73%)	795 (-99%)
Dry	93860 (-24%)	90890 (-27%)	24360 (-56%)	21390 (-61%)
Dodecane ($C_{12}H_{26}$)	**Heating Utilities (kW)**		**Cooling Utilities (kW)**	
	w/o Reactors	**w/ Reactors**	**w/o Reactors**	**w/ Reactors**
POX	22510 (-71%)	775 (-99%)	66090 (-45%)	44360 (-63%)
SR	142400 (-19%)	133400 (-24%)	9383 (-95%)	422 (-100%)
ATR	43710 (-57%)	1028 (-99%)	57850 (-51%)	15170 (-87%)
Methanol (CH_3OH)	**Heating Utilities (kW)**		**Cooling Utilities (kW)**	
	w/o Reactors	**w/ Reactors**	**w/o Reactors**	**w/ Reactors**
SCWR	389700 (-46%)	389700 (-46%)	3352 (-99%)	3352 (-99%)

Table 1: Results from process integration analysis (large scale production).

For large scale production, supercritical methanol reformation yields the highest heating demands for both of the reactor scenarios. Furthermore, steam reformation yields the lowest cooling demands and the second highest heating demands for both methane and dodecane. For methane, auto thermal reformation has the lowest heating demands; while, for dodecane the lowest heating demands are required by partial oxidation. Since auto thermal reformation combines the heat production of partial oxidation with the endothermic steam reformation, it is not surprising that it has the most opportunities for energy integration.

Methane (CH_4)	Heating Utilities (Kw)		Cooling Utilities (kW)	
	w/o Reactors	w/ Reactors	w/o Reactors	w/ Reactors
POX	183 (-68%)	28 (-95%)	161 (-73%)	6 (-99%)
SR	1276 (-18%)	1178 (-25%)	102 (-74%)	4 (-99%)
ATR	122 (-83%)	3 (-100%)	278 (-53%)	8 (-98%)
Dry	994 (-23%)	939 (-28%)	244 (-55%)	189 (-65%)

Dodecane ($C_{12}H_{26}$)	Heating Utilities (kW)		Cooling Utilities (kW)	
	w/o Reactors	w/ Reactors	w/o Reactors	w/ Reactors
POX	225 (-71%)	8 (-99%)	661 (-45%)	444 (-63%)
SR	1424 (-19%)	1334 (-24%)	94 (-78%)	4 (-99%)
ATR	437 (-57%)	10 (-99%)	578 (-50%)	151 (-87%)

Methanol (CH_3OH)	Heating Utilities (kW)		Cooling Utilities (kW)	
	w/o Reactors	w/ Reactors	w/o Reactors	w/ Reactors
SCWR	7093 (-47%)	7093 (-47%)	34 (-99%)	34 (-99%)

Table 2: Results from process integration analysis (small scale production).

For small scale production, again supercritical methanol reformation yields the highest heating demands for both of the reactor scenarios. Supercritical methanol yields the lowest cooling demands when the reactors are only matched with external utility streams; however, when the reactors are matched internally the lowest cooling demand is required by steam reformation. For methane auto thermal reformation yields the lowest heating demands for both reactor scenarios and has the highest cooling demands when the reactors are only matched externally. When the reactors are only matched internally, auto thermal reformation has the second highest cooling demands. For dodecane, steam reformation yields the highest heating demands; conversely, this reformation strategy also yields the lowest cooling demands. Again, auto thermal reformation has the largest potential for energy integration, due to the combination of heat production from partial oxidation and endothermic steam reformation.

In addition, two more scenarios for supplying external heating utilities were investigated for each of the reforming models. One scenario provides external heating utilities through the combustion of a fraction of the individual fuel source; while the other utilizes the combustion of natural gas to generate the necessary external heating. These two scenarios were modeled to assist in the evaluation of the raw material's cost; a significant part of the total economical analysis. Lastly, an economical analysis was conducted to evaluate the overall hydrogen production cost for each of the reformation strategies. The reformation models that utilized methane as the combustion fuel an allowed the reactors to be matched with internal utility streams were determined to be the most cost efficient. This is primarily due to the lower fuel cost of methane and the lower utility requirements to be supplied by external utilities. The following figures illustrate the percentage make-up of the total production cost for each of the most cost efficient reformation models. Figures 26-31 represent the three primary reformation strategies fueled by dodecane and methane, figure 31 represents supercritical reforming fueled by methanol, and figure 33 represents dry reforming fuel by methane.

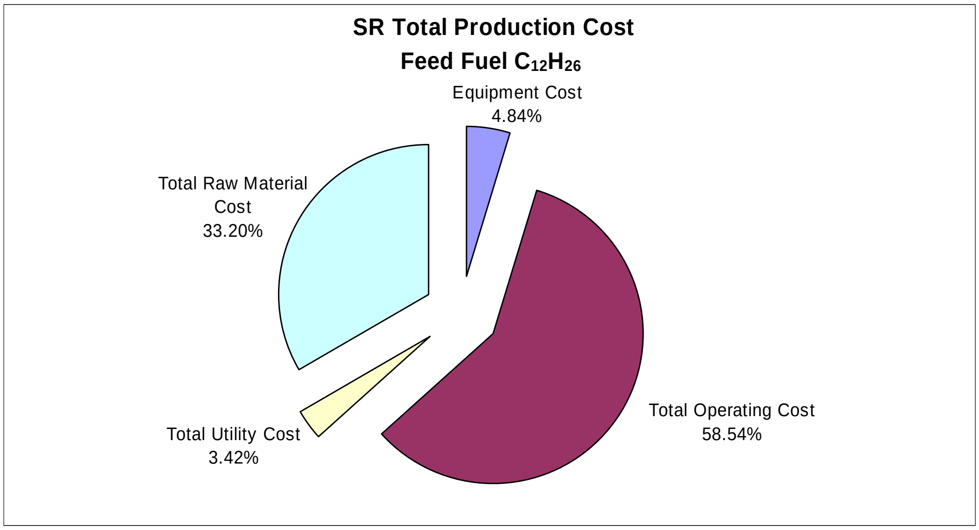


Figure 26. $C_{12}H_{26}$ Steam reforming (SR) Total Production Cost Analysis

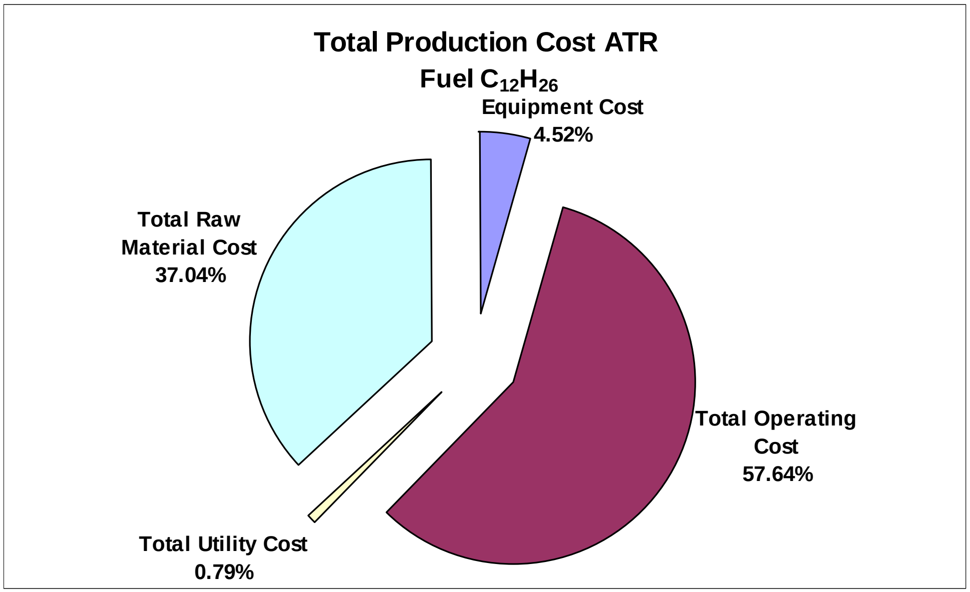


Figure 27. $C_{12}H_{26}$ Auto Thermal reformation (ATR) Total Production Cost Analysis

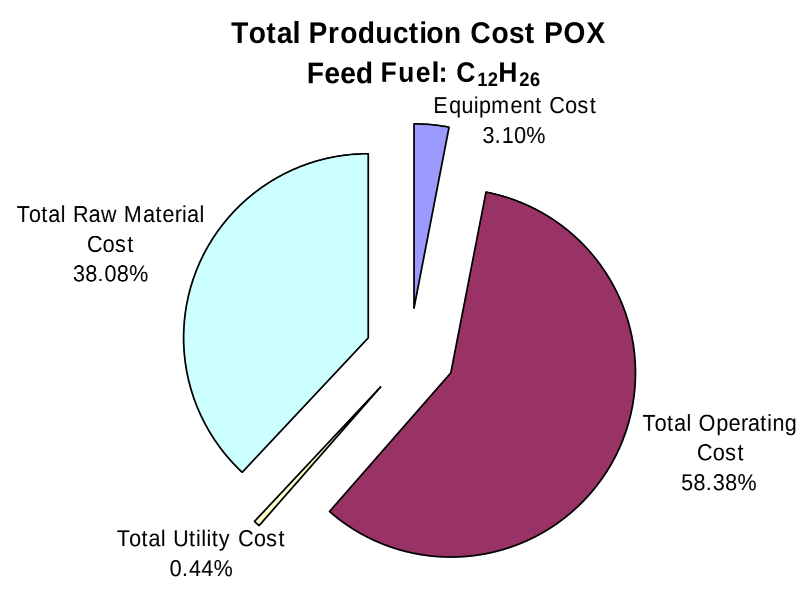


Figure 28. $C_{12}H_{26}$ Partial Oxidation (POX) Total Production Cost Analysis

For the three primary reformation models that utilize dodecane as the feed fuel the main costs arise from the total operating and raw material cost; while, the total utility and equipment cost contribute to only a small percentage of the total production cost. An increase in the raw material cost would have a significant impact on the total production cost of these reformation strategies.

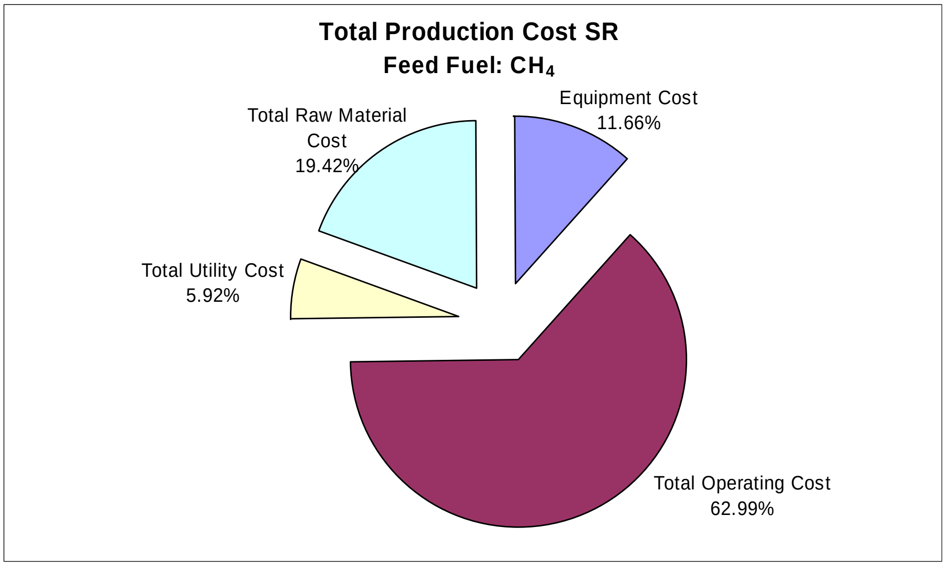


Figure 29. CH_4 Steam reforming (SR) Total Production Cost Analysis

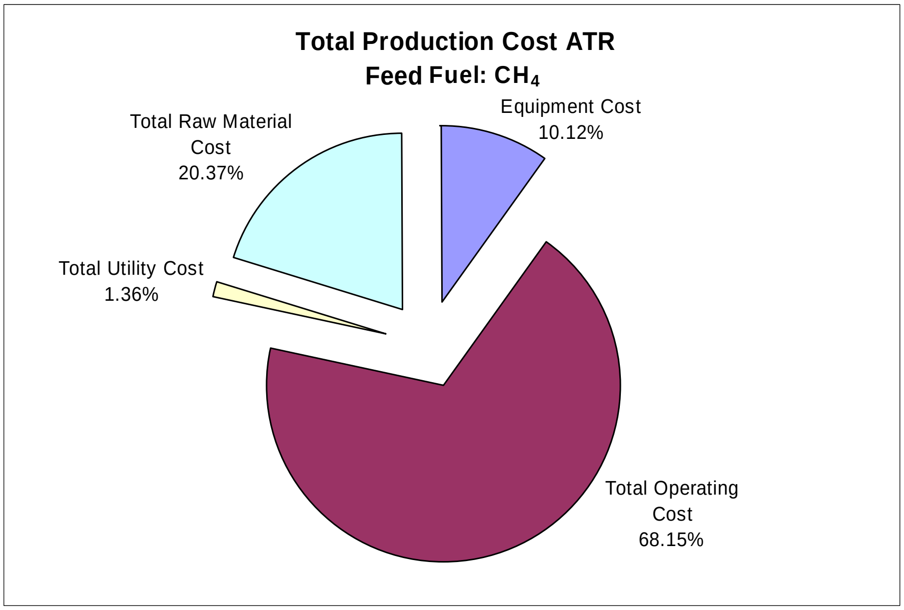


Figure 30. CH_4 Auto Thermal reformation (ATR) Total Production Cost Analysis

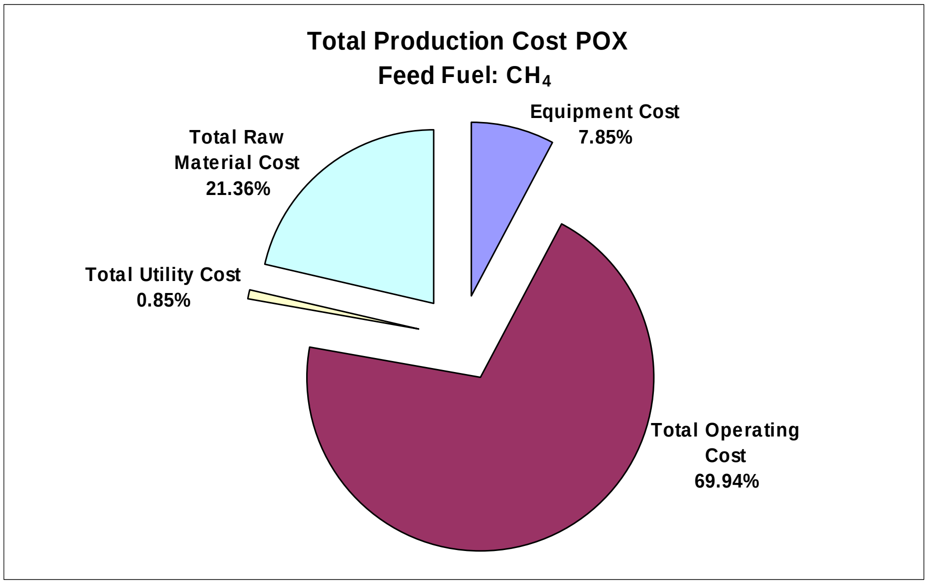


Figure 31. CH_4 Partial Oxidation (POX) Total Production Cost Analysis

For the three primary reformation models that utilize methane as the feed fuel the main costs arise from the total operating and raw material cost; while, the total utility and equipment cost contribute to only a small percentage of the total production cost. However, the equipment cost has a greater impact on the total cost for these reformation strategies fueled by methane than when they are fueled by dodecane. Again, an increase in the raw material cost would have a significant impact on the total production cost of these reformation strategies.

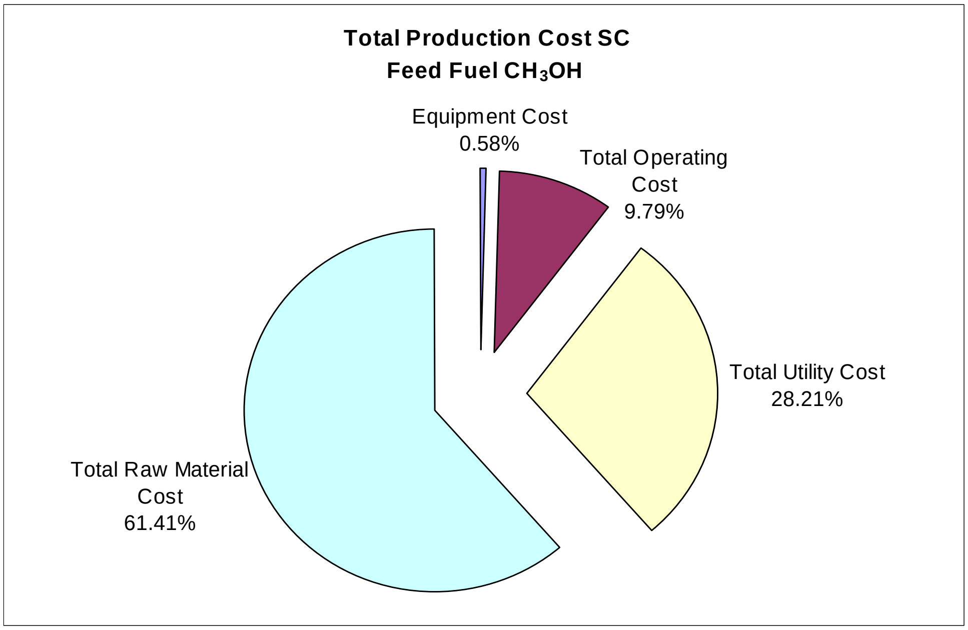


Figure 32. Supercritical (SC) Methanol reforming Total Production Cost Analysis

The total production costs for the supercritical methanol reforming are primarily influenced by the raw material cost. The utility costs have the second largest impact on the total production cost. The equipment cost and the total operating cost have a minor impact on the total production cost for these reformation strategies.

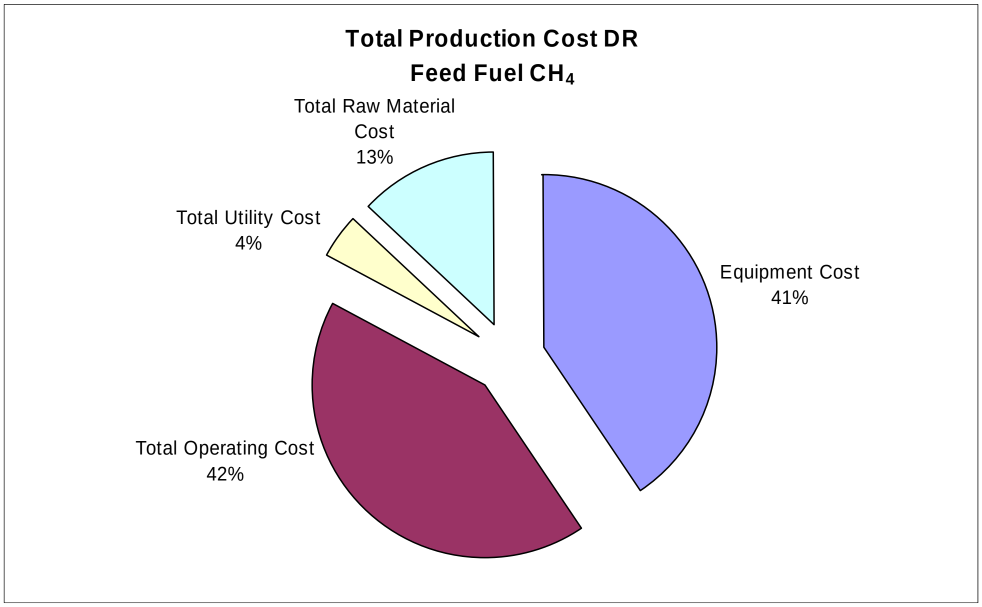


Figure 33. Dry (DR) Methane reformation Total Production Cost Analysis

The total production costs for the dry methane reforming are primarily influenced by the total operating and equipment costs. The utility costs have a minimum impact on the total production cost. An increase in raw material cost would have the least impact on the dry methane reforming compared to all other reformation strategies.

The total production costs were then normalized using the results for steam reforming of natural gas, which is the prevailing means of producing hydrogen. The results are shown in figure 34. In figure 34, the first three processes represent the traditional reforming strategies (SR, POX, ATR) for natural gas, while the remaining processes represent dry reforming (DR) of natural gas, reforming diesel fuel using SR, POX, ATR respectively, and finally supercritical water reforming (SCWR) of methanol. The results show it is apparent that dry reforming is the only technology that could be economically feasible for comparison with today's steam reforming.

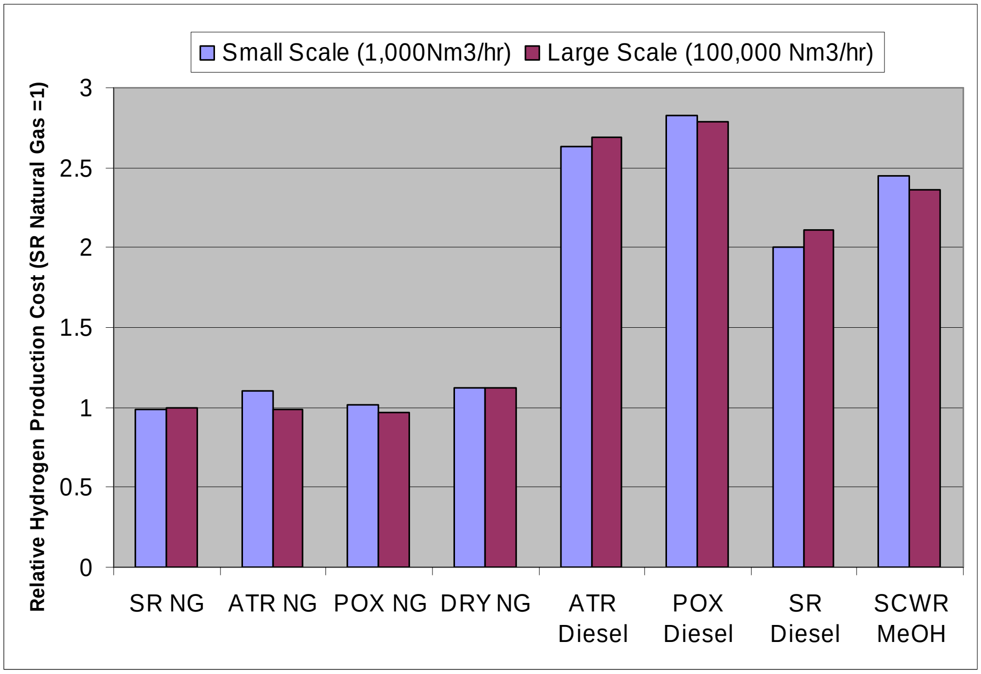


Figure 34: Relative hydrogen production cost

9. ANALYSIS OF HYDROGEN PRODUCTION UNDER SIZE CONSTRAINTS

9.1. Introduction

Minimizing the size of the process system in terms of weight and volume as well as the footprint size for the desired electricity production are the two primary concerns when selecting a reformation strategy that is capable of being utilized for mobile applications. Reformation models were simulated for the three primary reforming strategies: steam reforming (SR), auto thermal reforming (ATR), and partial oxidation (POX). Each reformation model was evaluated with multiple hydrocarbon fuels to investigate the effects of fuel complexity on the system. Methane was utilized to represent natural gas; while, dodecane was employed to signify diesel fuel. The JP-8 jet fuel was represented by a combination of C_{10}, C_{12}, C_{14}, and C_{16}, given that these four components characterize approximately 80% of the jet fuel.

The heat exchanger network area is related directly to the weight and indirectly to the volume of the fuel. The weight to fuel correlation is illustrated by the requirement for larger areas as the flow rates are increased; while, the volume to fuel correlation is represented by the algebraic relationships that relate density, volume, and weight.

The comparison of the minimum utility requirements and the opportunity to apply integration potentials are key factors that are evaluated, when determining the best reformation strategy for each specific hydrogen application. The utility requirements of the system reflect specifically on the reformation strategy, given that the post-reformer clean up steps have equal utility requirements.

9.2. Simulation Results

Heating and cooling duties, and the reformer and the water gas shift (WGS) reactor effluents were extracted from the simulation models. Table 3 displays the minimum heating and cooling duties, the integration potential, the amount of hydrogen produced, and the electric current generated by the fuel cell. All the values reported in table 3 were calculated by Aspen Tech and Aspen HX-Net.

Methane CH_4	**SR**	**POX**	**ATR**
Min. Heating (kW) [% reduction]	20,240 [36%]	1,996 [80%]	1,820 [83%]
Min. Cooling (kW) [% reduction]	1,987 [85%]	3,702 [68%]	2,827 [76%]
H_2 Production (mol)	247	172	175
Electric Current (10^4 A)	3.81	2.65	2.7

Dodecane $C_{12}H_{26}$	**SR**	**POX**	**ATR**
Min. Heating (kW) [% reduction]	19,560 [37%]	6,767 [56%]	6,618 [61%]
Min. Cooling (kW) [% reduction]	2,170 [84%]	2,678 [76%]	1,798 [85%]
H_2 Production (mol)	215	130	134
Electric Current (10^4 A)	3.32	2.00	2.07

Reduced JP8	**SR**	**POX**	**ATR**
Min. Heating (kW) [% reduction]	18,210 [36%]	6,717 [56%]	6,643 [61%]
Min. Cooling (kW) [% reduction]	1,638 [86%]	2,668 [76%]	1,795 [85%]
H_2 Production (mol)	215	130	134
Electric Current (10^4 A)	3.31	2.01	2.07

Table 3. Summary of integration potential of fuel reforming models

The two main achievements of this work are the comparison of reformation strategies based on their utility requirements and energy integration potential and the development of relationships between volume and weight size constraints with electricity production, HEN area, and the complexity of fuels (Cummings, 2006).

Both literature and this work show that the highest hydrogen production, thus the most electricity production occurs with steam reformation (Brown, 2001). Consequently, even though steam reforming produces the highest yield of hydrogen, it also requires the highest heating utilities of the three primary reformation strategies. Auto thermal reforming has the lowest heating and second lowest cooling requirements. Partial oxidation has the second lowest heating requirements; however, it also has the highest cooling requirements of all the proposed reformation strategies. Figure 35 illustrates the relationships between the HX-Net design areas and the electrical production of the various reformation strategies and the multiple reforming fuels; in addition, this figure evaluates the optimum combination of reforming fuel and strategy to achieve the best energy utilization. When attempting to achieve the optimum energy utilization of a process, the two primary constraints on the system are the size of the heat exchanger networks and the minimum electrical production requirements of the process. Both of these concerns can be evaluated using the data in figure 35.

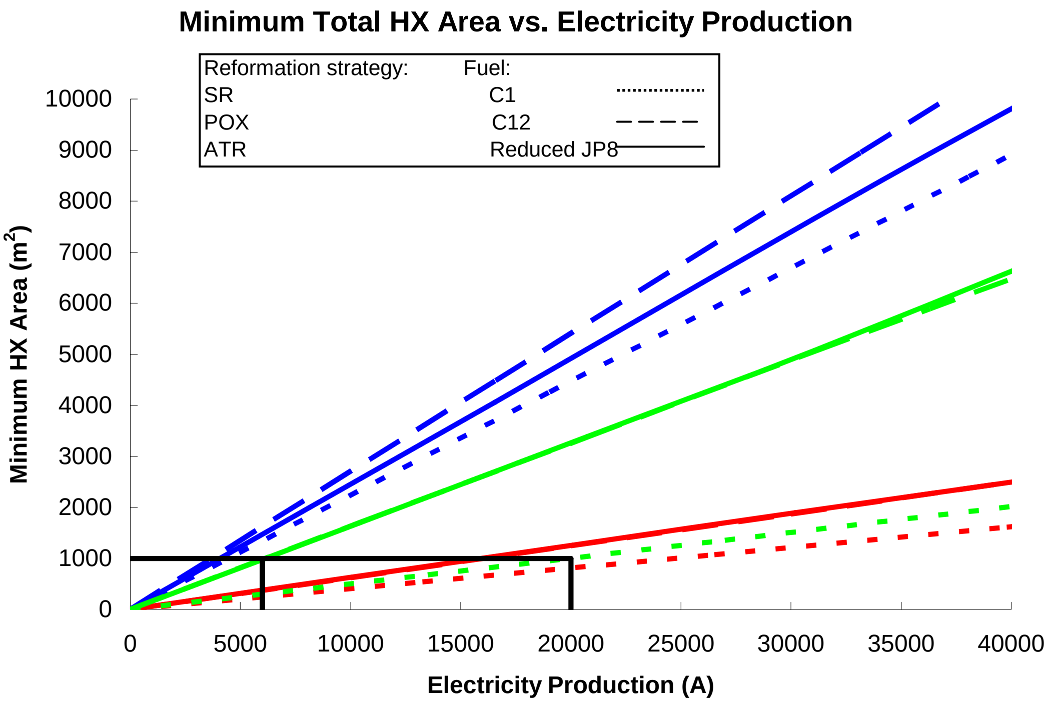


Figure 35. HX area and electricity production for best energy utilization

Auto thermal reforming was evaluated on the basis of energy utilization, since the data generated confirms that the ATR reformation strategy has the lowest heating and second lowest cooling requirements as well as the largest opportunity for potential integration for the multiple reforming fuels that were investigated.

Placing a constraint of 1,000 m^2 on the maximum heat exchanger network will yield a maximum power generation of 20,000 A by utilizing methane as the fuel; however, employing dodecane or JP-8 as the reformation fuel will provide only 6,000 A of generated power. Conversely, if the process system has a minimum electricity production requirement of 20,000 A, the minimum area for a sufficient heat exchanger network is 1,000 m^2 for methane and approximately 3,000 m^2 for JP-8 and dodecane.

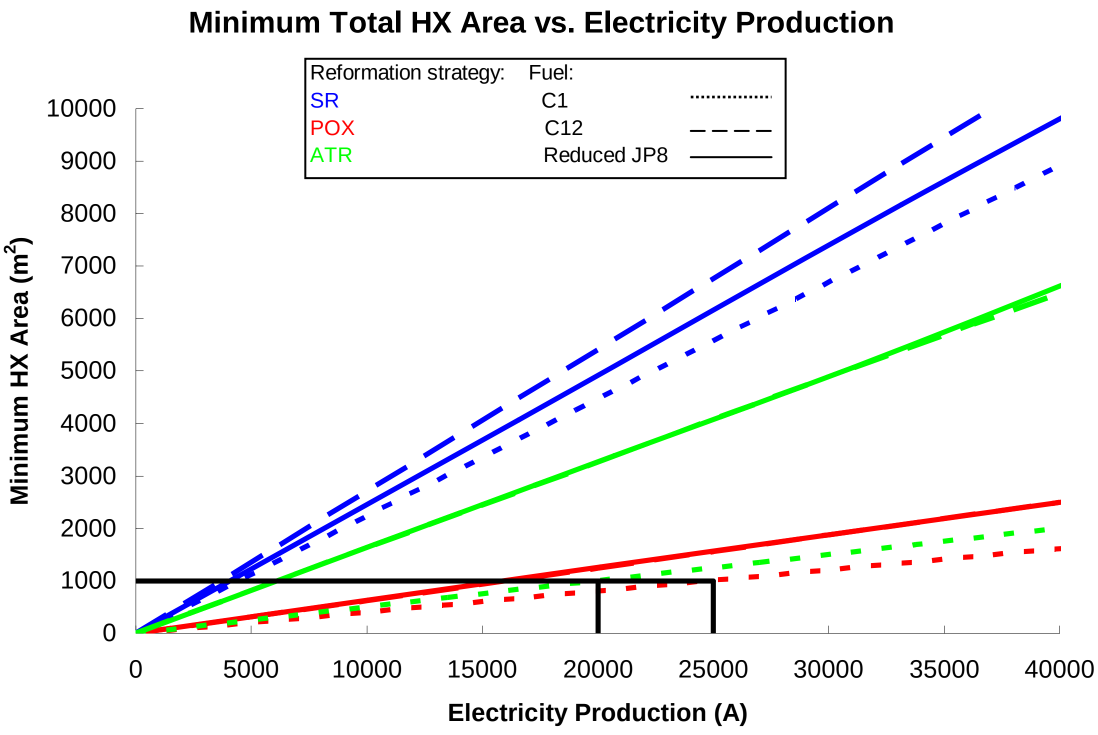


Figure 36. HX area and electricity production for maximum power production

If the consideration is no longer energy utilization, but rather how to achieve maximum power for a fixed size, the relationships in figure 35 may be extended to those shown in figure 36. Utilizing methane as the reforming fuel, auto thermal reforming has the capabilities of producing a maximum of 20,000 A of power under a size constraint of 1000 m^2. Partial oxidation has the ability to produce a maximum of 25,000 A of power, which is 5,000 A more than produced by auto thermal reforming, under an equal size constraint and employing the same reforming fuel. The trade-offs between size, reformation strategy, and power must be evaluated in order to determine the optimal system.

The data from the simulation models can also be utilized to develop relationships between the fuel storage volume and the electricity production. Figure 37 graphically illustrates the quantity of electricity that is capable of being generated by a certain reformation strategy for a precise volume of fuel that is fed. Methane, due to having a much larger vapor volume than liquid hydrocarbons, is positioned on a different axis than dodecane and the JP-8.

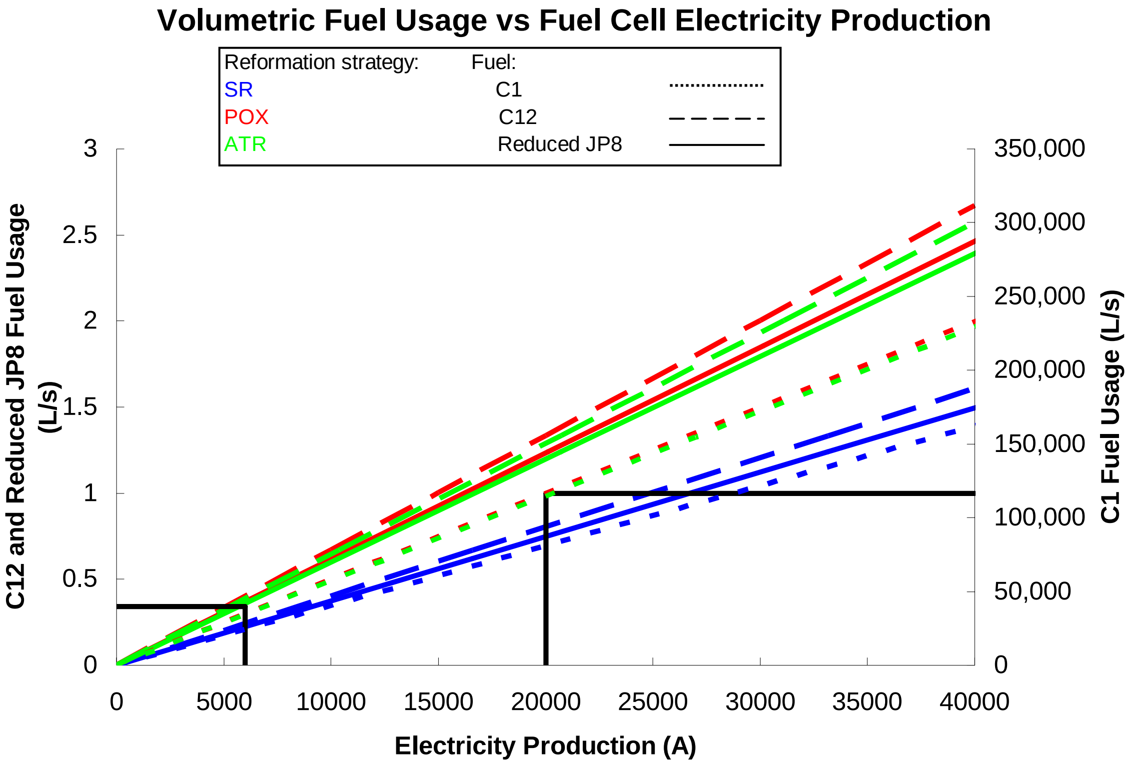


Figure 37. Relationship between fuel storage volume and electricity production

Utilizing the auto thermal reformation strategy to produce 20,000 A of electricity would require storage facilities of roughly 120,000 L/s for the vapor fuel; while the storage requirements for the liquid hydrocarbons would be approximately 0.34 L/s for the electricity production of 6000 A. Employing a liquid hydrocarbon fuel instead of a hydrocarbon vapor fuel would reduce the required storage volume from 120,000 L/s to 1.3 L/s, for a auto thermal reformation process with a minimum power production requirement of 20,000 A. The more complex liquid hydrocarbon fuels use less volume of fuel; however, the power production is significantly lower than when a vapor hydrocarbon fuel is utilized. These relationships enable a better understanding of the effects on the process design depending on whether the constraint is on process size, storage limits or electricity production.

These relationships may be used to design the process for a given constraint, given that the optimization targets of the heat exchangers and which fuel and reformation strategy combination supplies the most power production has already been identified. If the system is constrained by the fuel storage volume, as in mobile applications, the maximum power will be obtained from the more complex hydrocarbon fuels. However, if the system is constrained by the weight instead of the storage volume of the fuel, the maximum power will be achieved by the lower hydrocarbon fuels. These relationships may have been theoretically obvious before; nevertheless, they have now been quantified for specific fuels and reformation strategies.

10. CONCLUSIONS

10.1. Achievements

The main achievement of this work is the holistic comparison of the reformation strategies based on the impact of their utility requirements, energy integration potential, equipment costs, and raw material costs on the total production cost. The results from the economic analysis allow the reformation strategies to be evaluated for a specific hydrogen application and determine which strategy is the most suitable for that specific application. Also, relationships between volume and weight size constraints with electricity production, HEN areas, and the complexity of fuels were developed to evaluate the potential of each reformation strategy for mobile applications.

The success of the future hydrogen energy economy is largely dependent on cost competitiveness of hydrogen with other transportation fuels. The ability to produce hydrogen cheaply is only the first of many challenges that need to be addressed. The implementation of a hydrogen energy infrastructure will require enormous investments in new production and distribution systems.

When evaluating reforming strategies for mobile applications on a basis of energy cost versus electricity production, auto thermal reformation is the fuel processing strategy of choice. Relationships between the electricity production and system constraints have been quantified to aid in the design of a fuels processing system for mobile applications. An increased understanding of how the maximum electricity generated by the fuel cell is fundamentally dependent on the limits of the fuel volume and mass as well as the footprint of the heat exchanger network area has also been achieved. Fuel volume storage constraints suggest reforming higher hydrocarbon fuels, while fuel weight constraints suggest lower hydrocarbon fuels. Minimizing heat exchanger network areas generally requires a lower hydrocarbon fuel for partial oxidation and auto thermal reformation; while, steam reforming footprint requirements are all much greater than the other reforming strategies.

Other achievements of this work include the development of simulation models of the entire fuels processing system and economic analysis for each reformation strategy. These models include five fuel reforming strategies and three different fuel sources, allowing for a greater understanding of the effects that increasing fuel complexity will have on the entire system. A simplified approach to the estimation of reformation kinetics has also been developed, allowing for the simulation of complex kinetics with simplified reaction stoichiometry. The economical analysis results allow each reformation strategy and reforming fuel to be evaluated and allocated to a specific hydrogen application in which that strategy has the most suitable performance.

It is apparent that the current technologies for producing hydrogen from liquid fuels are not attractive if evaluated only on the production costs. Benefits such as storage, transportability, etc. will need to be quantified for all types of fuel in order to better compare the technologies. However, dry reforming technology appears to be a potentially cheaper alternative to the current state of the art. These results provided from this work, challenges previous ideas on how to compare the value of each reformation strategy.

The results obtained in this work indicate that for industrial scale production of hydrogen, only dry reforming (DR) of natural gas shows any promise for competing with the traditional reforming strategies like steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). For size-constrained systems, e.g. onboard vehicular fuel processing systems, partial oxidation appears to provide the best trade-off between power production and system size.

10.2. Remaining Challenges & Future Work

This work is a small step in the work that must be completed in order to establish a future hydrogen energy economy. The implementation of a hydrogen energy infrastructure will require enormous investments in new production and distribution systems. A simplified approach was utilized in specifying fuels and reaction kinetics. Logistical fuels vary widely in their compositions, depending on their crude and refining sources. These particular modeling studies investigated three logistical fuels: natural gas, diesel, and methanol. In order to develop the basic reformation relationships, minor simplification of the logistical fuels was necessary. Natural gas was simplified as methane, while dodecane provided a simple representation of diesel fuel. More models, with specific detail on the logistical fuels, should be investigated to better understand the effects of fuel composition on the energy integration potential of the process system. Similarly in this work, complex reaction kinetics were represented by simplified stoichiometric equations. Yet again, more work is necessary to broaden the understanding and advance the development of the reaction equations which is a critical component for the construction of efficient reformers. As to date there has been no detailed kinetic work reported concerning the exact break down of complex hydrocarbon fuels during reformation. Currently, due to insufficient kinetic data, process adjustments are made in temperature, pressure, and feed ratios to obtain high hydrogen yields. A thorough understanding of the reformation kinetics of complex hydrocarbon mixtures will greatly impact the fuels processing industry.

Besides developing more complex, detailed models of fuels and fuels processing, research into alternative fuels appears promising. The search for environmentally friendly energy resources has moved into reforming bio-derived fuels, such as ethanol, Fischer-Tropsch liquids, bio-diesel and di-methyl-ether (DME). Bio-derived fuels have energy densities comparable to other hydrocarbon fuels and are renewable unlike fossil fuels (Ullmann's, 2003).

This analysis focused on five reformation strategies, chosen for the extensive work and research previously completed on the processes. These various reforming strategies have been found to satisfy the requirements of both large and small scale stationary production as well as mobile and portable applications (quick start up, produces adequate quantities of hydrogen, etc.) and their energy requirements are well known. Evaluating other reformation strategies, i.e. plasma and non-oxidative catalytic dehydrogenation of alkanes, may provide opportunities in energy management, overall production costs, electricity production, and storage/transportation limitations, which may make it possible to overcome current reformation difficulties. Plasma reforming utilizes microwaves with air and steam to remove hydrogen from gasoline. Non-oxidative catalytic dehydrogenation employs enzymes or microwave pulses to separate hydrogen from alkanes. These and other reformation strategies will need to be further investigated and compared with current technologies.

Evaluating alternative reforming fuels and strategies will provide more information on how to produce the most hydrogen in a cost effective, environmentally friendly manner for various applications. Seeing that one of the main challenges of the future hydrogen energy economy is the cost reduction of hydrogen production, more reformation models will need to be generated and investigated to compare the cost analysis of the different reforming strategies. Various reforming fuels should also be evaluated to achieve a relationship between raw material and production cost, to ensure the process system is reaching the highest hydrogen conversion for the least raw material cost. Also energy integration should be investigated and employed to reduce the utility cost, which have a major impact on the total production cost. At the current time the cost of hydrogen production for transportation fuels is not competitive with conventional fuels and technologies. The cost of hydrogen, regardless of the production technology, must be competitive with gasoline prices. Further research is needed to significantly reduce the capital equipment, operational, and maintenance costs; in addition, to improving the efficiency of hydrogen production technologies and addressing the environmental emission issues.

Further research is also needed in developing a storage and transportation infrastructure; which is another challenging area of for the future hydrogen energy economy. There is no current storage or transportation infrastructure that is capable of supplying the quantity of hydrogen needed for automotive and off-board applications from production sites to end users. Additional investigation should be completed to evaluate decentralized and centralized hydrogen production; along with, evaluating which reformation strategy and infrastructure is most applicable for each specific hydrogen application. Along with hydrogen production technologies, the storage and transportation infrastructure is a major obstacle that must be overcome to ensure the success of the future hydrogen energy economy.

Further size constrained work should be completed for solid oxide, molten carbonate, or other types of fuel cells to achieve the same electricity production from the fuel cells while decreasing the equipment and energy requirements to clean-up reformer effluent; thus also reducing the production costs. Advancement in these research and development areas would enable tremendous potential for utilizing these methods in mobile application and other size-limited application such as microelectronics, aviation, space and submarines.

This work has developed preliminary methods to perform economic analyses for each of the reformation strategies and fuels. The methods apply specifically to evaluating the fuel processing cost and assessing means of reducing these costs. More models need to be developed and data provided to create a standard approach to optimizing a process system under economic constraints of energy integration and process equipment and raw material cost standpoints.

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