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PROJECT ADMINISTRATION DATA SHEET

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Project No. E-25-611 (R5987-0A0) GTRC/~~GIT~~ DATE 7 /23 /85

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Sponsor: Battelle Memorial Institute
Pacific Northwest Laboratories

Type Agreement: Contract B-04024-A-V

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	This Change	Total to Date
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Title: Development of an Innovative Concept for a High Temperature Heat Pump

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Date 3/12/86

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oject Director(s) S.M. Jeter GTRC / GIT

onsor Battelle

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- [ ] None
- [X] Final Invoice or Final Fiscal Report Fixed Price
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1.0 Innovative High-Temperature Heat Pump

1.1 Concept Assessment

1.1.1 Description

An economical high-temperature heat pump could have wide application throughout the chemical process industries. In many cases where high-temperature endothermic reactions are employed, a high-temperature heat pump could be integrated into the system. Example applications are the production of ethylene and benzene which are the principal building blocks of the petrochemical industry. Another example is the production of high heating-value fuel gas from coal.

If brought into practice the high-temperature heat pump could have several benefits:

1. Reduce the consumption of primary fuels for process heating or for the provision of energetic feedstock.

2. Provide new flexibility for synergestic process improvements such as heat recovery and cogeneration of power and heat.

3. Allow for the substitution of high-quality fuels, especially petroleum and natural gas, by a much lower quantity of electrical power produced from less-limited coal or nuclear resources.

To operate at high temperatures, a heat pump will require a revolutionary approach if it is to be both efficient and reliable. Conventional concepts require complex and critical rotating machines, pumps and compressors and turbines, to compress and expand the working fluid. It is unrealistic to expect that such machines can be developed which can operate for years at temperatures c. 1000K with the reliability needed in an industrial environment and at the costs demanded in a competitive economy. The concepts described herein will exploit a fundamental advance in material science, the development of refractory solid electrolytes than can conduct sodium ions. This material introduces a revolutionary new type of energy conversion device, a solid-state compressor or expander which has no moving parts and is largely immune to degradation at high temperatures.

According to Boercker (1979) around 45% of industrial process heat is required at temperatures exceeding 350^{o}C. Provision of heat at such temperatures requires a heat pump that can operate with a high temperature source since it would be futile to attempt to supply high temperature process heat by a heat pump operating with the surroundings as the source. Even an ideal Carnot cycle heat pump using an ambient source in a representative application (T_H = 350^oC and T_L = 20^oC) would have a COP of only 1.89. Using the national average net electrical conversion and transmission efficiency as reported by the U.S. Energy Information Administration (1982), of 29.3%, results in an overall energy efficiency of only 55.3%. Consequently, a heat-pump without a high-temperature source would not promote more efficient energy use.

The opportunity for energy conservation while improving or maintaining industrial productivity comes from process improvements allowed by this concept. An example application is shown in Figure 1. Gasification of coal or char is used as the example only because the details of this process are widely reported. The conceptual high-temperature heat pump would of course be applicable to processes other than the production of fuel gas from coal. This process is, however, representative of the many potential applications throughout the chemical process industry. In the example a highly endothermic reaction such as

$$C + H_2O \quad H_2 + CO$$

proceeds at an elevated temperature. In conventional gasfiers, which operate without catalysts, a temperature of c. 1250K is required because of kinetic limitations. With a suitable catalyst, see Hirsch, et al (1982), temperature c. 975K is adequate. An exothermic reaction (here the "water gas shift" and "methanation" reactions) is also required to produce the desired product via the overall reaction

$$2H_2 + 2\ CO \rightarrow CH_4 + CO_2\ .$$

The methanation and shift can be accomplished at temperatures c. 700K, according to Hirsch, et al (1982). The mismatch in temperatures between the lower-temperature energy-releasing operation and the higher-temperature energy-absorbing operation is typical of many industrial processes. This problem may be ameliorated by interposing a heat pump between the two reactors. One heat pump concept is shown in Figure 2. Such a heat pump must be reliable and efficient at very high temperatures. Only non-conventional

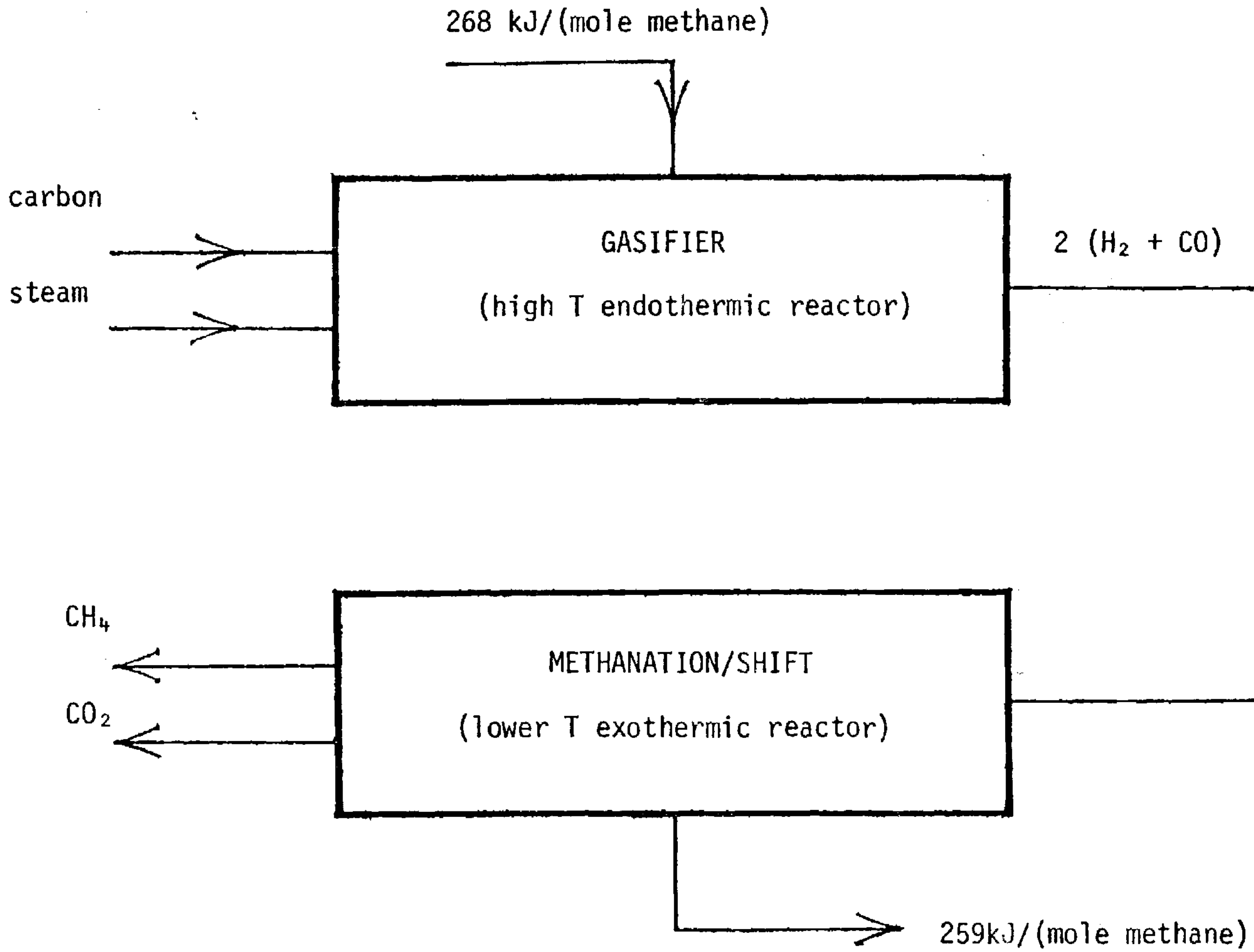


Figure 1: A Representative Candidate Process for a High-Temperature Heat Pump Application

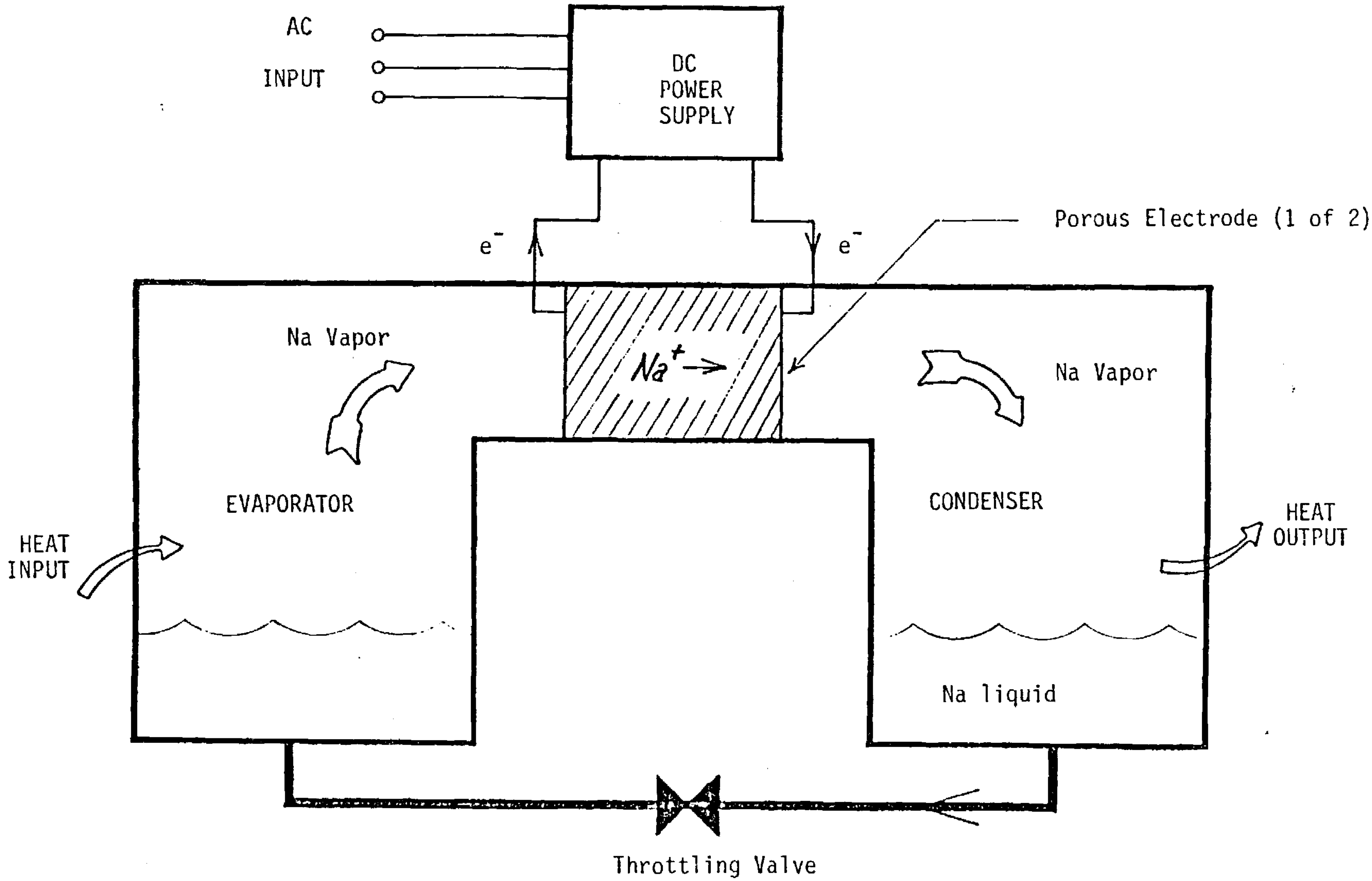


Figure 2: Schematic of High-Temperature Heat Pump

concepts can meet this criterion.

While several theoretical cycles are thermodynamically feasible, all share the same salient innovative aspect, the component used for compression and, in some cycles, expansion. In the familar vapor-compression cycle, a conventional system would use a motor-driven compressor. Such rotating equipment is expensive and unreliable at elevated temperatures. The innovative concept is to use a solid state device, specifically a solid electrolyte coated with a porous electrode to convey the working fluid, an alkali metal. The resulting heat pump system will be hardly more complex than a common heat pipe or indirect heat exchanger.

The proposed heat pump requires no moving parts and thus circumvents the imposing problems presented to the development of reliable and economical very high temperature turbines, compressors, and seals. For example, current practice limits central utility turbines to approximately 870K which is well below the temperatures envisioned here. The innovative heat pump relies on the unique ability of the beta-aluminum solid electrolyte (commonly known as BASE) to transport sodium ions. The high-temperature heat pump employing BASE is both conceptually and mechanically simple. Illustrated in Figure 2 is a high-temperature heat pump operating on the vapor-compression cycle. In construction, this heat pump is hardly more complicated than a simple heat pipe. In operation, Na is vaporized in the lower-temperature evaporator. Na atoms are absorbed on a porous electrode (anode) covering the BASE where they give up an electron. The electrons are pumped by the DC power supply to the cathode (another porous conductive layer). The Na^+ ions are attracted to the cathode and migrate freely through the polycrystalline structure of the BASE. After recombination Na atoms are at a higher electrochemical potential consistent with the higher pressure and temperature in the condenser. The Na vapor then condenses giving up heat to the high-temperature process. The liquid Na is returned via a pressure-reducing valve to the evaporator. If a circulating pump is required an electromagnetic pump can be used; consequently the Na is contained in an hermetically-sealed system with no requirement for rotating shaft seals.

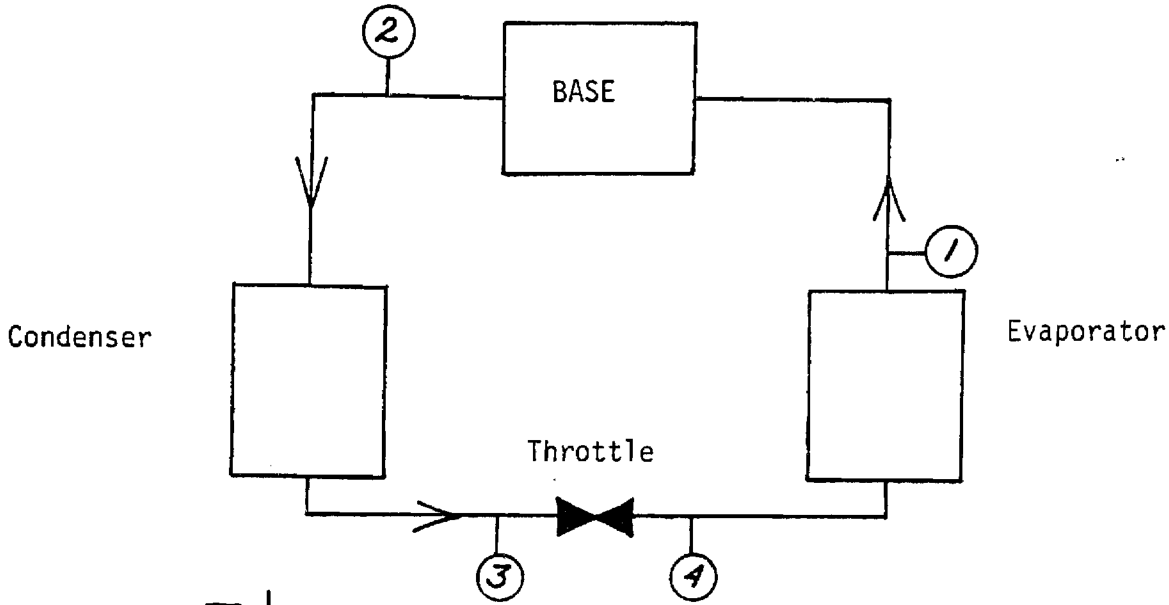
Considerable work has already been accomplished both in materials development and in the development of analytical tools and engineering data which can be applied to this concept. Much of this work stems from efforts to develop the alkali-metal thermoelectric convertor (AMTEC) converter for space and other remote applications, as described by Weber (1974) and Cole (1983). Overall one can state that the basic technology is well established including the structure and performance of the BASE and porous electrodes. The technology for the routine use and handling of liquid metals, is also well established and has been competed by Foust (1972). It is interesting to note that since the AMTEC cycle includes an isothermal expansion from saturated liquid to superheated vapor at the highest temperature in the cycle, a simple reversed-AMTEC cycle is not feasible as a heat pump.

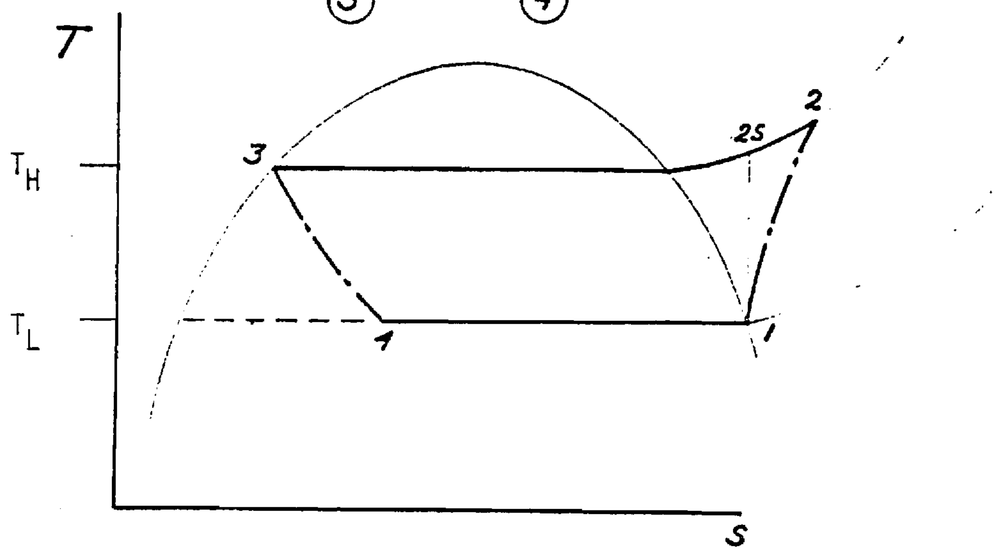
Because of its simple, sealed design the high-temperature heat pump should be simple, reliable, and potentially inexpensive. While the presence of a vessel filled with Na vapor is understandably awe-inspiring, it must be recalled that any high-temperature vapor is dangerous and that Na is less so than many because of its low vapor pressure (1 atm at 1155K).

The thermodynamic cycle for the high-temperature vapor-compression system is shown in Figure 3. Constant-pressure evaporation is followed by adiabatic compression (by action of the DC-circuit on the ion transport in the BASE) and constant-pressure condensation at higher temperature. Constant-enthalpy throttling of the liquid completes the cycle. The table accompanying Figure 3 gives results for representative temperatures using an isentropic "compression efficiency" of 90%. The attainable "compression efficiency" depends on the quality, area, and thickness of the BASE and the performance of the AC/DC converter. The value of 90% yields a system COP of 6.53. Using the average electrical-conversion efficiency of 29.3% results in an overall COP of 1.91. The resultant energy and cost savings are obvious; and since the power source would be a modern base-load coal or nuclear plant, environmental degradation would be less than from on-site burning.

The vapor-compression cycle appears to have one significant problem. As illustrated in Figure 2, the lower pressure face of the BASE is exposed to vapor at the lowest temperature in the cycle, T_L, while the higher pressure face is exposed to vapor at the highest temperature, T_H. This dictates that a substantial temperature difference must exist across the BASE. The resulting heat conduction opposes the energy flow induced by the heat pump cycle. This degradation of performance has no analog in the conventional fluid cycle. Depending on the design geometry the performance reduction caused by this "heat leak" could be serious.

In addition to the high temperature analog to the vapor-compression cycle





Temperature/Entropy Diagram

station	$T(^oK)$	S(kJ/kg K)	h(kJ/kg)
1	950	4.6085	4360.5
2s	1488	4.6085	5008.8
2			5080.8
3	1082		379.6
4	950		379.6

$$COP = \frac{q_H}{w} = \frac{5080.8 - 379.6}{5080.8 - 4360.5} = 6.53$$

Figure 3: Thermodynamic Model and Analysis

discussed above, analogs to cycles that are thermodynamically more promising are possible because of the flexibility of BASE as an energy input or output component. In particular, the reversed Brayton heat pump cycle could be considered. In this concept BASE would be used to perform both the work input, compression, process and the work output, expansion, process. Another especially exciting prospect is an application of the Ericsson cycle. In the Ericsson cycle both the work input process and the work output processes are to be conducted isothermally. Because of the practical difficulties in exchanging heat to or from a fluid while it flows through a conventional turbocompressor or turboexpander, the Ericsson cycle is largely hypothetical so long as one is limited to conventional turbomachines. However, so long as ions are flowing through the crystalline matrix of a BASE expander or compressor they are in intimate contact with a solid. Heat transfer to the "ionic fluid" during expansion and from the fluid during compression becomes not only possible using BASE but possibly desirable to reduce the required heat exchange surface. Since the reversible Ericsson cycle achieves the Carnot efficiency, it is possible that a high temperature heat pump operating on a practical Ericsson cycle could attain a very high COP. Additionally, since the expansion and compression components are isothermal, the "heat leak" problem inherent in the vapor-compression cycle is avoided.

A rough calculation allows an estimate of the performance of a reversed Ericsson cycle heat pump. For the source temperature of $950^{o}K$ and supply temperature of $1082^{o}K$ a reversed Carnot heat pump would have as its COP the fundamentally limiting value:

$$COP = \frac{T_H}{T_H - T_L} = \frac{1082^{o}K}{1082^{o}K - 950^{o}K} = 8.2$$

A practical cycle cannot attain so high a COP being limited by the finite temperature differences required for economically-sized heat exchangers and by component efficiencies. If ideal-gas behavior is assumed for simplicity, the COP of a practical Ericsson cycle heat pump is given by the formula:

$$COP = \frac{T_H/n_c - (1-\varepsilon)\dfrac{T_H - T_L}{\ln(P_H/P_L)}}{T_H/n_c - n_e T_L}$$

where: η_c = "compressor" efficiency
η_e = "expander" efficiency
ε = heat exchanger effectiveness

As with similar "gas cycles" the COP of the Ericsson cycle is sensitive to component efficiencies because of the large "negative work" (i.e. compression work input) of the cycle. If, however, very efficient BASE converters become available the Ericsson cycle would be a strong alternative to the vapor-compression cycle. For example with 1082^0K supply and 950^0K source and 95% component efficiencies the COP could reach 4.82, nearly as good as the vapor-compression cycle.

1.1.2 Potential Energy Savings and Other Benefits

The potential energy savings and other benefits of the high-temperature heat pump are to be found not in the traditional "energy industries" such as electric utilities and space heating and comfort conditioning but in the chemical process industry which is largely an energy conversion industry in disguise.

An example is the production of ethylene (ethene), $H_2C = CH_2$. The double bond makes ethylene highly reactive allowing it to be converted to numerous end products. Ubiquitous versions of polyethylene and familiar compounds like ethylene glycol attest to the fact that ethylene is the favorite building-block of the petrochemical industry. As a consequence of its importance for the production of various polymers and other compounds, ethylene is the most widely produced organic chemical.

Actual ethylene plants are quite intricate and highly integrated to facilitate heat recovery and other energy economics. Since a realistic plant is too complicated for detailed consideration here, a simplified model will be used to illustrate the problems in energy engineering in the chemical process industry which could be somewhat assuaged if an economical high temperature heat pump were available.

Ethylene is usually produced by the high-temperature decomposition (dehydrogenation by pyrolysis) of hydrocarbon raw material from natural gas or petroleum. At the risk of oversimplification, the process will be modeled as the dehydrogenation of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

This strongly endothermic process is usually carried out around 1100K. The overall process is illustrated in the temperature-enthalpy diagram shown in Figure 4 which has been constructed for one kilomole (kg-mole) of ethylene. Process 1-2 is the preheating of the hydrocarbon, ethane, feedstock. This is followed, process 2-3, by high-temperature pyrolysis. The products are cooled to ambient temperature in process 3-4. In the production of a kilomole of ethylene, the preheating of the reactant, a kilomole of ethane, requires c. 77,600kJ. This is greatly exceeded by the sensible enthalpy in the products, a kilomole of ethylene and a kilomole of hydrogen, amounting to c. 109,000kJ. Unless some convenient heating load is available a minimum of around 29% of the sensible enthalpy in the products must be lost.

A situation employing simple heat recovery via a recouperating heat exchanger is illustrated in Figure 4.b. For a heat exchanger of realistic size not even all the preheat can be delivered by heat recovery. Heat recovery would stop at point a, no more than 80% to 90% of the preheat required. The additional preheat must be provided by burning expensive high-quality fuel in the pyrolysis furnace.

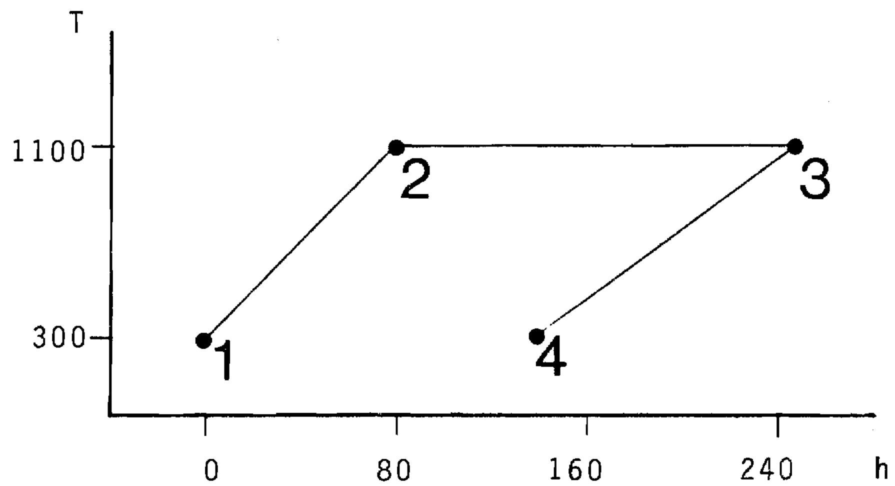
The potential for process improvement is illustrated in Figure 4.c. Here all the sensible enthalpy of the product stream is recovered by interposing a system of high-temperature heat pumps between that stream and the pyrolysis section and reactant stream. In addition, the energy of the net work input to the heat pumps is also supplied to the process.

As illustrated in this example potential benefits include energy savings, especially in processes involving high-temperature endothermic reactions, and other benefits such as:

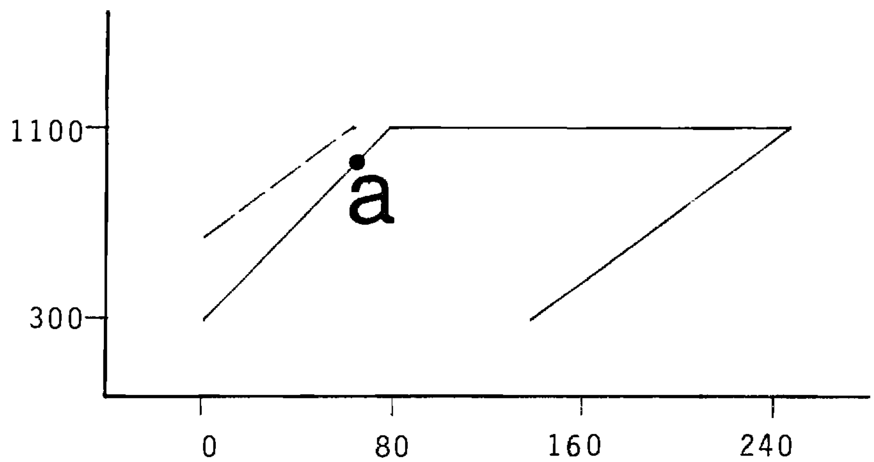
1. Reduced thermal pollution and cooling water consumption in heat rejection.

2. Straightforward energy conservation avoiding the need for extensive plant integration which is expensive in construction, imposing on plant maintenance and operation, and inflexible to market demands and to the cost of competing fuels.

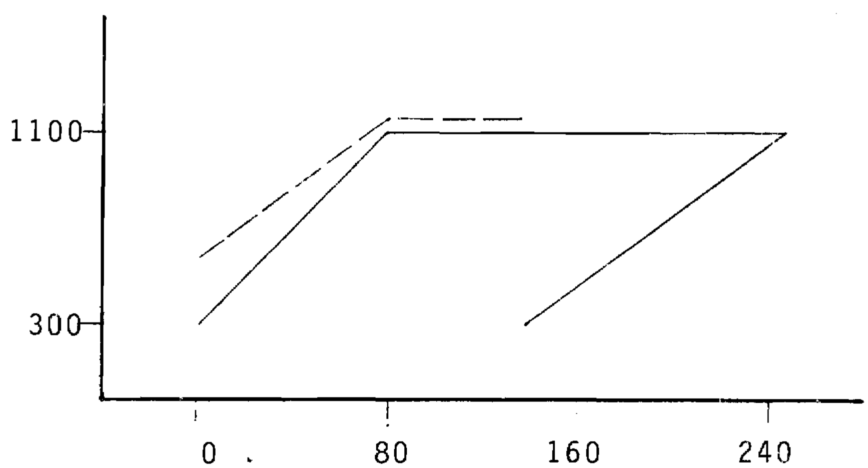
3. Allow for electrofication of processes that now require on-site burning. Expensive fuels can be displaced by cheaper coal and nuclear resources. Environmental degradation can be minimized by extensive abatment



(a) Ethylene Production by Pyrolysis of Ethane



(b) Ethylene Production with Simple Heat Recovery



(c) Ethylene Production using BASE Heat Pump

Figure 4. Temperature (T, Kelvin) versus Enthalpy (h, MJ/kmole) Diagrams for Ethylene Production

measures possible at the central utility facility.

1.1.3 Technical Feasibility and Impediments to Deployment

As illustrated in the previous calculations, a high-temperature heat pump employing BASE is thermodynamically feasible. While other thermodynamic cycles will be sought and considered, both the vapor-compression cycle and reversed Ericsson cycle are promising candidates. Certain technical questions remain. The effect of the contrary conduction of heat in the BASE on the performance of the vapor-compression cycle is crucial. Since the Ericsson cycle is rather more complicated requiring BASE components for compression and expansion as well as an internal recouperating heat exchanger, component efficiencies and effectiveness will have a marked effect on the performance of the system.

A more detailed thermodynamic and transport model for the candidate systems will be required so that their performance can be assessed in potential applications. Such performance results can be combined with costs analysis to determine the economical benefit of a BASE heat pump.

Certain external factors could inhibit the deployment of the BASE heat pump. At present, the production levels of petrochemicals may be stagnant. New capacity coming into operation may be in oil-producing countries where local fuel costs are arbitrarily low. This situation, especially in view of today's "oil glut", may discourage the construction of new plants that could use BASE heat pumps or the modification of existing plants.

An additional possible impediment may be rigidities in the detailed chemical processing. For example, ethylene is unstable at high temperatures. Consequently, in conventional processing, the hydrocarbon feedstock is rapidly heated and the product rapidly cooled or quenched. These very high heating rates may be incompatible with economical heat pumps.

1.1.4 Current Technology

The technology for energy - conversion devices employing BASE as heat engines (usually referred to as AMTEC, alkali-metal thermoelectric converters, or SHE, sodium heat engine, technologies) are well developed as outlined by Cole (1983) and Subramanian and Hunt (1983). The SHE might be deployed for nuclearpower in space, as a topping cycle in coal-fired central electric plants, or in modular-dish solar thermal power can exploit this technology.

The principal "competitor" to BASE heat pumps is the current pratice of thermal energy management in process synthesis and plant design. Ingenious methods including heat recovery, cogeneration, and reaction combination are features of today's highly integrated process plants. The BASE heat pump can be considered as an additional tool in plant integration. For example a BASE heat pump can be used to overcome unfavorable temperature differences and facilitate high-temperature heat recovery. Alternatively, contrast BASE may allow less well integrated plants to be energy efficient. This could save capital and allow more flexible response to the market demands.

1.2 Research and Development Needs

1.2.1 Immediate Needs

The most pressing needs are to demonstrate that BASE heat pumps are technically feasible and that economically advantageous applications exist. In the current research, the following tasks will be pursued to fill those needs:

1. Development of thermodynamic and transport models for the BASE heat pump concepts.
2. Survey application in important sectors of the chemical process industries.
3. Develope projected cost and performance data and economic evaluations.
4. Present the results of work to the technical community.

1.2.2 Longer Term Need

Development of BASE heat pumps will not occur unless an organization with the requisite technical and financial resources undertake a campaign of research, development, and demonstration. It is felt that if postive results are obtained from the current research the foundation will be established to market this concept to capable firms. The important resources of the Georgia Tech Research Corporation and the Georgia Tech Advanced Technology Research Center are available to facilitate this activity.

E-25-611

Innovative High-Temperature Heat Pump

by
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(Prepared on NBI System)

ABSTRACT

Research on an innovative high-temperature heat pump is described. The preferred concept is a high-temperature analog to the familar vapor-compression cycle. The concept is innovative in that a solid state component, beta-alumina solid electrolyte (or BASE), is used to perform the compression function. This concept promises to be reliable and efficient at the high temperatures required for many applications in the chemical process industries. The economic viability of the concept depends on the relative costs of electric power to energize the BASE compressor compared with alternative fuels for direct heating, but the BASE heat pump could be an attractive alternative.

1.0 Innovative High-Temperature Heat Pump

1.1 Concept Assessment

1.1.1 Description

An economical high-temperature heat pump could have wide application throughout the chemical process industries. Likely applications include those involving high-temperature endothermic reactions which are typical in the production of energetic monomers such as ethylene and benzene, the principal building blocks of the petrochemical industry. A high-temperature heat pump could be used to recover energy from the hot products. Often a high-temperature endothermic reaction (e.g. to produce an energetic intermediate product) is associated with a somewhat lower-temperature exothermic reaction. In such a situation a high-temperature heat pump could be advantageously integrated into the system. An example is the production of high heating-value fuel gas from coal.

If brought into practice the high-temperature heat pump could have several benefits:

1. Reduce the consumption of primary fuels for process heating or for the provision of energetic feedstock.

2. Provide new flexibility for synergistic process improvements such as heat recovery and cogeneration of power and heat.

3. Allow for the substitution of high-quality fuels, especially petroleum and natural gas, by a much lower quantity of electrical power produced from less-limited coal or nuclear resources.

To operate at high temperatures, a heat pump will require a revolutionary approach if it is to be both efficient and reliable. Conventional concepts require complex and critical rotating machines, pumps and compressors and turbines, to compress and expand the working fluid. It is unrealistic to expect that such machines can be developed which can operate for years at temperatures c. 1000K with the reliability needed in an industrial environment and at the costs demanded in a competitive economy. The concepts described herein will exploit a fundamental advance in material science, the development of refractory solid electrolytes than can conduct sodium ions. This material introduces a revolutionary new type of energy conversion device, a solid-state compressor or expander which has no moving parts and is largely immune to degradation at high temperatures.

According to Boercker (1979) around 45% of industrial process heat is required at temperatures exceeding 350°C. Provision of heat at such temperatures requires a heat pump that can operate with a high temperature source since it would be futile to attempt to supply high temperature process heat by a heat pump operating with the surroundings as the source. Even an ideal Carnot cycle heat pump using an ambient source in a representative application (T_H = 350°C and T_L = 20°C) would have a COP of only 1.89. Using the national average net electrical conversion and transmission efficiency as reported by the U.S. Energy Information Administration (1982) of 29.3%, results in an overall energy efficiency of only 55.3%. Consequently, a heat-pump without a high-temperature source would not promote more efficient energy use.

The opportunity for energy conservation while improving or maintaining industrial productivity comes from process improvements allowed by this new concept. An example application is shown in Figure 1. The gasificaton of coal or char is used as an example only since the details of this process have been widely reported in conjunction with the development of synthetic fuels technology. The conceptual high-temperature heat pump would of course be applicable to processes other than the production of fuel gas from coal. This process is, however, representative of the many potential applications throughout the chemical process industry where endothermic and exothermic reactions are coupled. In the example a highly endothermic reaction such as

$$C + H_2O \quad H_2 + CO$$

proceeds at an elevated temperature. In conventional gasifiers, which operate without catalysts, a temperature of c. 1250K is required because of kinetic limitations. With a suitable catalyst, see Hirsch, et al (1982), temperature c. 975K is adequate. An exothermic reaction (here the "water gas shift" and "methanation" reactions) is also required to produce the desired product via the overall reaction

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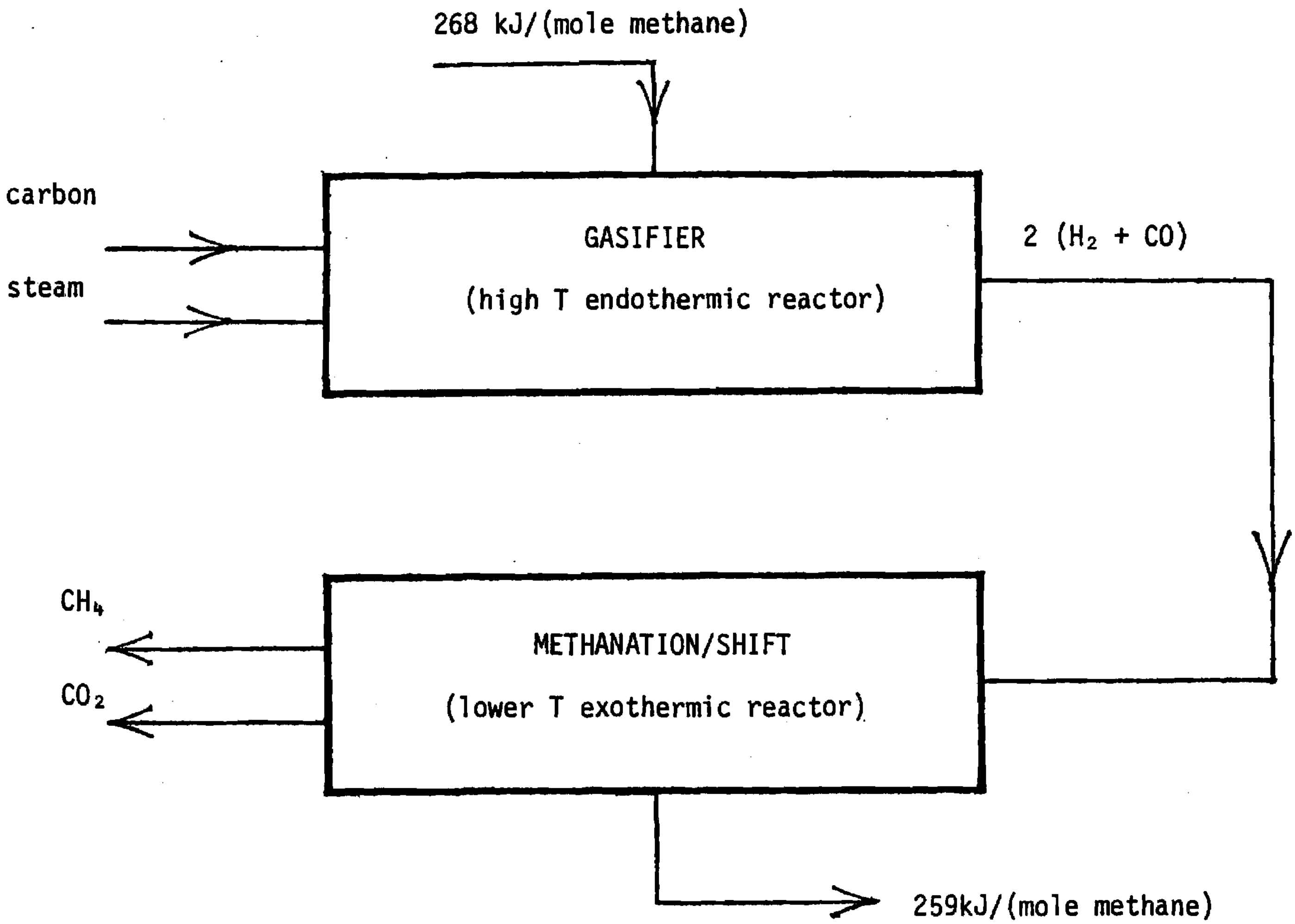

Figure 1 A Representative Candidate Process for a High-Temperature Heat Pump Application

energy-absorbing operation is typical of many industrial processes. This problem may be ameliorated by interposing a heat pump between the two reactors. Such a heat pump must be reliable and efficient at very high temperatures. Only non-conventional concepts can meet these criteria.

While several theoretical cycles are thermodynamically feasible, all share the same salient innovative aspect, the component used for compression and, in some cycles, expansion. In the familar vapor-compression cycle, a conventional system would use a motor-driven compressor. Such rotating equipment is expensive and unreliable at elevated temperatures. The innovative concept is to use a solid state device, specifically a solid electrolyte coated with a porous electrode to convey the working fluid, an alkali metal.

The proposed heat pump requires no moving parts and thus circumvents the imposing problems presented to the development of reliable and economical very high temperature turbines, compressors, and seals. For example, current practice limits central utility turbines to approximately 870K which is well below the temperatures envisioned here. The innovative heat pump relies on the unique ability of beta-alumina solid electrolyte (commonly known as BASE) to transport sodium (Na) ions. The high-temperature heat pump employing BASE is both conceptually and mechanically simple. Illustrated in Figure 2 is a high-temperature heat pump operating on the vapor-compression cycle. In construction, this heat pump is hardly more complicated than a simple heat pipe. In operation, Na is vaporized in the lower-temperature evaporator. Na atoms are absorbed on a porous electrode (anode) covering the BASE where they give up an electron. The electrons are pumped by the DC power supply to the cathode (another porous conductive layer). The Na^+ ions are attracted to the cathode and migrate freely through the polycrystalline structure of the BASE. After recombination Na atoms are at a higher electrochemical potential consistent with the higher pressure and temperature in the condenser. The Na vapor then condenses giving up heat to the high-temperature process. The liquid Na is returned via a pressure-reducing valve to the evaporator. If a circulating pump is required an electromagnetic pump can be used; consequently the Na is contained in an hermetically-sealed system with no requirement for rotating shaft seals.

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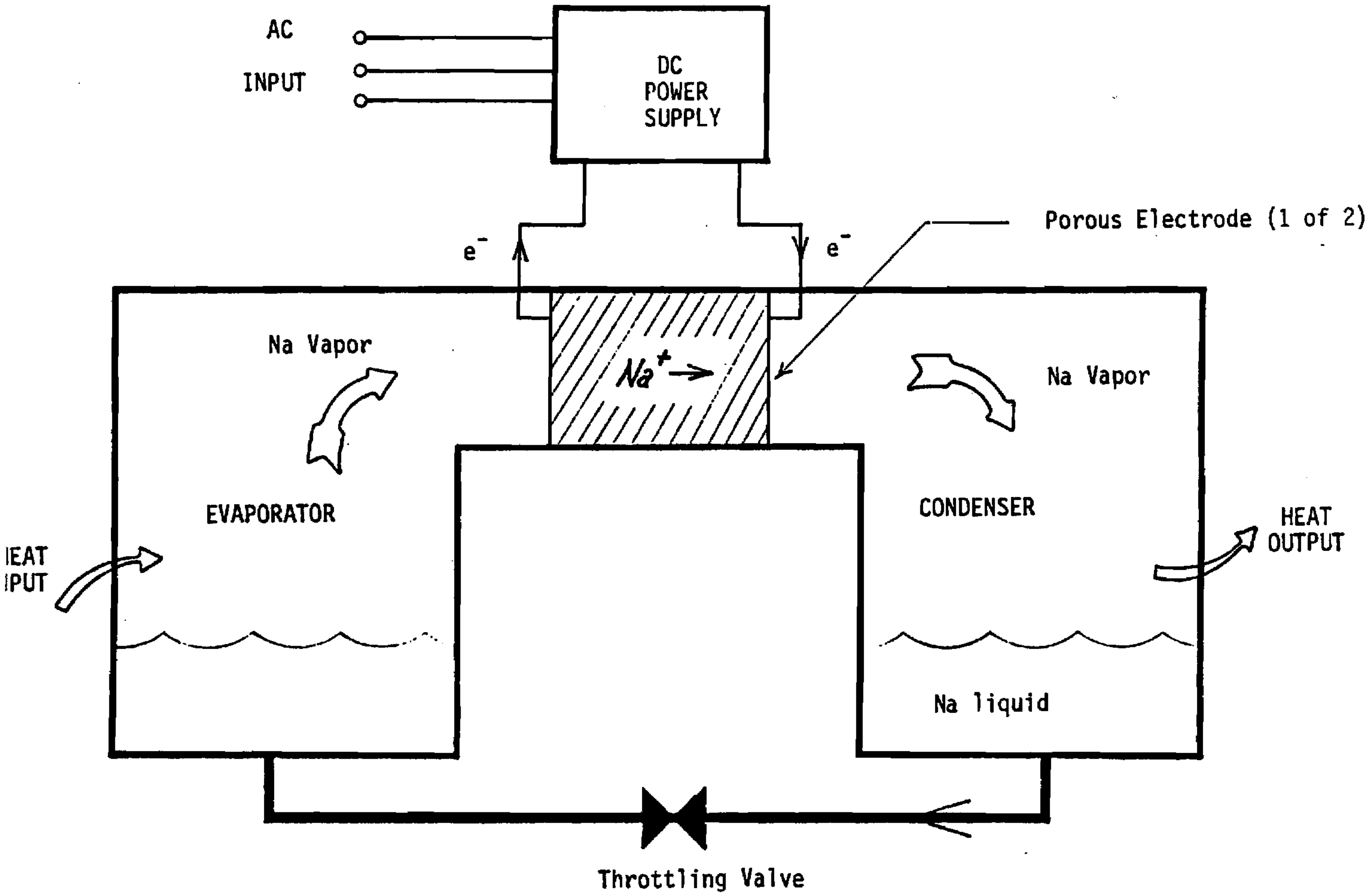


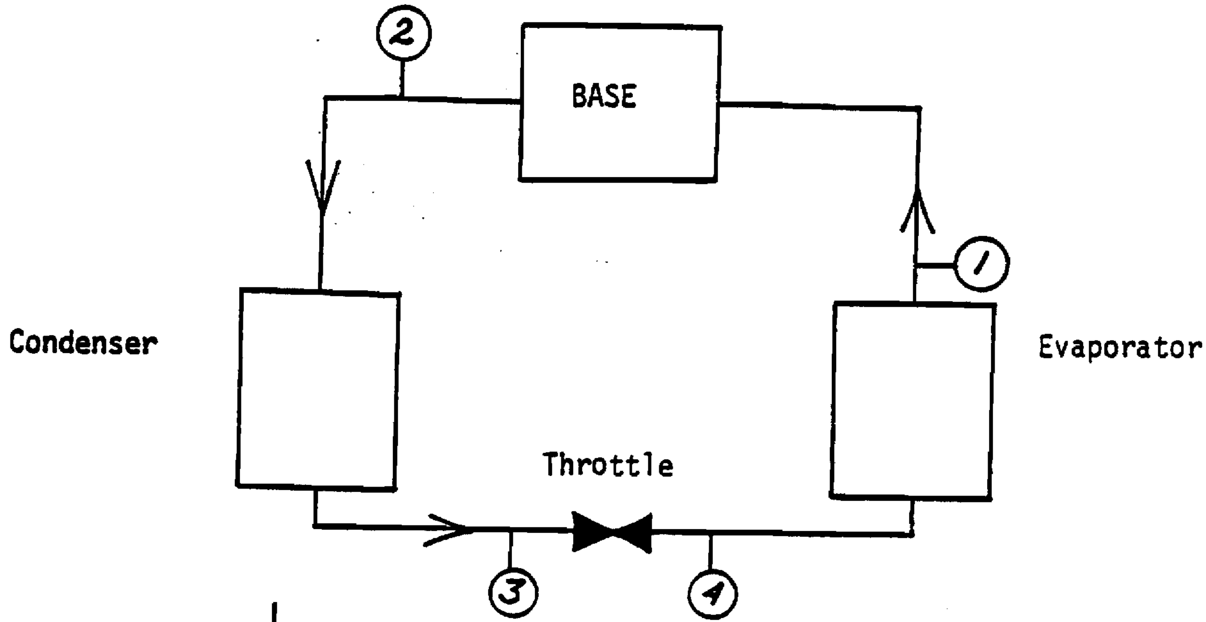
Figure 2. Schematic of High-Temperature Heat Pump Using Vapor Compression Cycle

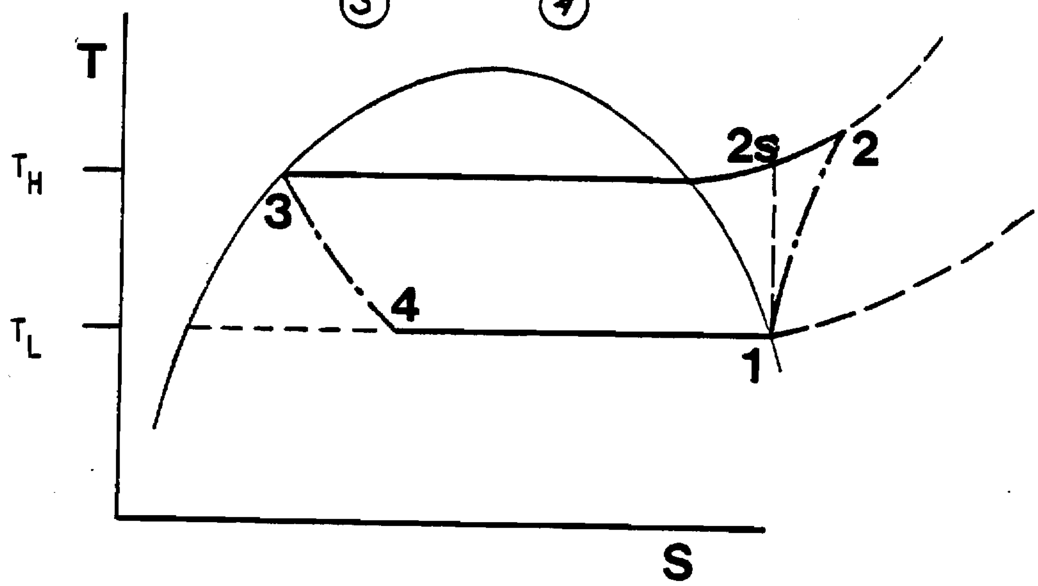
which can be applied to this concept. Much of this work stems from efforts to develop the alkali-metal thermoelectric convertor (AMTEC) converter for space and other remote and conventional applications, as described by Weber (1974) and Cole (1983). Overall one can state that the basic technology is well established, including the structure and performance of the BASE and porous electrodes. The technology for the routine use and handling of liquid metals is also well established and has been compiled by Foust (1972). It is interesting to note that since the AMTEC cycle includes an isothermal expansion from saturated liquid to superheated vapor at the highest temperature in the cycle, a simple reversed-AMTEC cycle is not feasible as a heat pump.

Because of its simple, sealed design the high-temperature heat pump should be simple, reliable, and potentially inexpensive. While the presence of a vessel filled with Na vapor is understandably awe-inspiring, it must be recalled that any high-temperature vapor is dangerous and that Na is less so than many because of its low vapor pressure (1 atm at 1155K).

The thermodynamic cycle for the high-temperature vapor-compression system is shown in Figure 3. Constant-pressure evaporation is followed by adiabatic compression (by action of the DC-circuit on the ion transport in the BASE) and constant-pressure condensation at higher temperature. Constant-enthalpy throttling of the liquid completes the cycle. The table accompanying Figure 3 gives results for representative temperatures using an isentropic "compression efficiency" of 90%. The attainable "compression efficiency" depends on the quality, area, and thickness of the BASE and the performance of the AC/DC converter. The value of 90% yields a system COP of 6.51. Using the national average electrical-conversion efficiency of 29.3% results in an overall COP of 1.91. The resultant energy and cost savings are obvious; and since the power source would be a modern base-load coal or nuclear plant, environmental degradation would be less than from on-site burning.

The vapor-compression cycle appears to have one significant problem. As illustrated in Figure 2, the lower pressure face of the BASE is exposed to vapor at the lowest temperature in the cycle, while the higher pressure face is exposed to vapor at the highest temperature. This dictates that a substantial temperature difference must exist across the BASE. The resulting heat conduction opposes the energy flow induced by the heat pump cycle. This degradation of performance has no analog in the conventional fluid cycle.





Temperature/Entropy Diagram

station	T(K)	S(kJ/kg K)	h(kJ/kg)
1	950	4.6085	4360.5
2s	1517	4.6085	5010.6
2	1591		5082.8
3	1082		379.8
4	950		379.8

$$COP = \frac{q_H}{w} = \frac{5082.8 - 379.8}{5082.8 - 4360.5} = 6.51$$

Figure 3. Thermodynamic Model and Analysis

Depending on the design geometry and the conductivity in the crystal lattice the performance reduction caused by this "heat leak" could be serious.

An additional consideration is that low temperature operation of a BASE heat pump is not feasible. The normal melting point of Na is 371K and at such temperature its vapor pressure is quite low. A pratical lower limit is probably no lower than 475K.

In addition to the high temperature analog to the vapor-compression cycle discussed above, analogs to other cycles are possible because of the flexibility of BASE as an energy input or output component. For example, the reversed Brayton heat pump cycle could be considered. In this concept BASE would be used to perform both the work input, compression, process and the work output, expansion, process. Another interesting prospect is an application of the Ericsson cycle. In the Ericsson cycle both the work input and the work output processes are to be conducted isothermally. Because of the practical difficulties in exchanging heat to or from a fluid while it flows through a conventional turbocompressor or turboexpander, the Ericsson cycle is largely hypothetical so long as one is limited to conventional turbomachines. However, as ions flow through the crystalline matrix of a BASE expander or compressor they are in intimate contact with a solid. Heat transfer to the "ionic fluid" during expansion and from the fluid during compression becomes not only possible using BASE but possibly desirable to reduce the required heat exchange surface. Since the reversible Ericsson cycle achieves the Carnot efficiency, it is possible that a high temperature heat pump operating on a practical Ericsson cycle could attain a very high COP. Additionally, since the expansion and compression components are isothermal, the "heat leak" problem inherent in the vapor-compression cycle is avoided.

A rough calculation allows an estimate of the performance of a reversed Ericsson cycle heat pump. For the source temperature of 950K and supply temperature of 1082K a reversed Carnot heat pump would have as its COP the fundamentally limiting value:

$$COP = \frac{T_H}{T_H - T_L} = \frac{1082K}{1082K - 950K} = 8.2$$

A practical cycle cannot attain so high a COP being limited by the finite temperature differences required for economically-sized heat exchangers and by component efficiencies. If ideal-gas behavior is assumed for simplicity, the COP of a practical Ericsson cycle heat pump is given by the formula:

$$COP = \frac{T_H/\eta_c - (1-\varepsilon)\,\frac{T_H - T_L}{\ln(P_H/P_L)}}{T_H/\eta_c - \eta_e\, T_L}$$

where: η_c = "compressor" efficiency

η_e = "expander" efficiency

ε = heat exchanger effectiveness

As with similar "gas cycles" the COP of the Ericsson cycle is sensitive to component efficiencies because the large work input (compression) must be largely compensated for by the large work output (expansion) of the cycle. Component inefficiencies both increase the work input and decrease the work output resulting in serious overall performance degradation. If, however, very efficient BASE converters become available the Ericsson cycle would be a strong alternative to the vapor-compression cycle. For example, with 1082K supply and 950K source and 95% component efficiencies, the COP could reach 4.82, nearly as good as the vapor-compression cycle.

At present it appears that the vapor-compression cycle promises better performance than the Ericsson cycle even though the ideal Ericsson cycle is thermodynamically preferable. This performance differential exists because the Ericsson cycle is more sensitive to its component efficiencies. It includes two BASE converters and a recouperating heat exchanger. The vapor compression cycle is much simpler and should be significantly less expensive. Unless the performance penalty of the non-isothermal operation of the BASE in the vapor-compression system is found to be excessive it would be favored on both the bases of cost and performance and would be certain to be the more economical design unless very efficient BASE converters were available. The tentative design concept is then the vapor-compression cycle.

1.1.2 Potential Energy Savings and Other Benefits

The potential energy savings and other benefits of the high-temperature heat pump are to be found not in the traditional "energy industries" such as electric utilities and space heating and comfort conditioning but in the chemical process industry which is largely an energy conversion industry in disguise.

An example is the production of ethylene (ethene), $H_2C = CH_2$. The double bond makes ethylene highly reactive allowing it to be converted to numerous end products. Ubiquitous versions of polyethylene and familiar compounds like ethylene glycol attest to the fact that ethylene is the favorite building-block of the petrochemical industry. As a consequence of its importance for the production of various polymers and other compounds, ethylene is the most widely produced organic chemical.

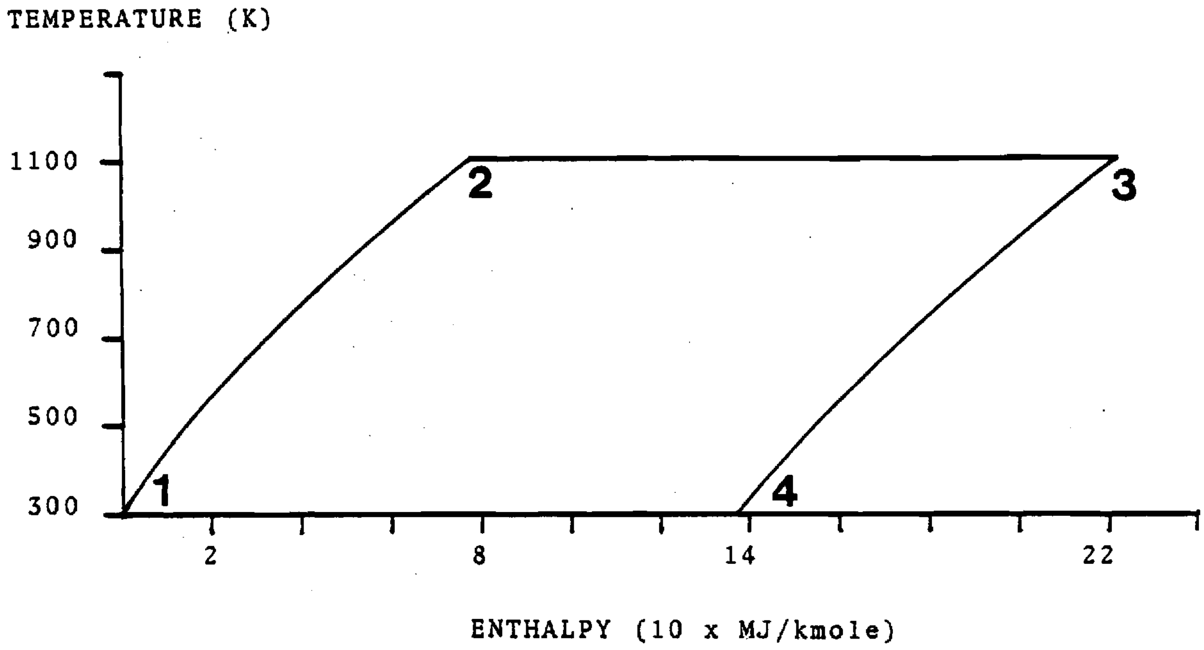
Actual ethylene plants are quite intricate and highly integrated to facilitate heat recovery and other energy economics. Since a realistic plant is too complicated for detailed consideration here, a simplified model will be used to illustrate the problems in energy engineering in the chemical process industry which could be somewhat assuaged if an economical high temperature heat pump were available.

Ethylene is usually produced by the high-temperature decomposition (dehydrogenation by pyrolysis) of hydrocarbon raw material from natural gas or petroleum. At the risk of oversimplification, the process will be modeled as the dehydrogenation of ethane:

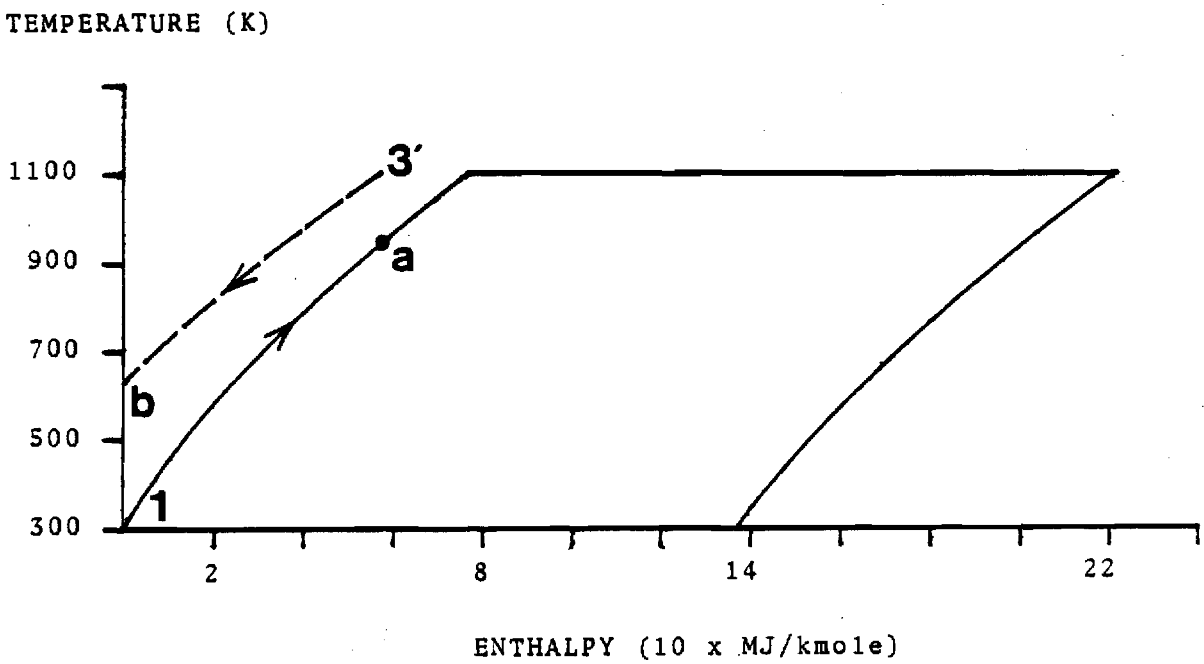
$$C_2H_6 \rightarrow C_2H_4 + H_2$$

This strongly endothermic process is usually carried out around 1100K. The overall process is illustrated in the temperature-enthalpy diagram shown in Figure 4 which has been constructed for one kilomole (kg-mole) of ethylene. Process 1-2 is the preheating of the hydrocarbon, ethane, feedstock. This is followed, process 2-3, by high-temperature pyrolysis. The products are cooled to ambient temperature in process 3-4. In the production of a kilomole of ethylene, the preheating of the reactant, a kilomole of ethane, requires c. 76,900kJ. This is greatly exceeded by the sensible enthalpy in the products, a kilomole of ethylene <u>and</u> a kilomole of hydrogen, amounting to c. 85,100kJ. Unless some convenient heating load is available a minimum of around 9.5% of the sensible enthalpy in the products must be lost.

A situation employing simple heat recovery via a recouperating heat exchanger is illustrated in Figure 4.b. For a heat exchanger of realistic size not even all the preheat can be delivered by heat recovery. Heat



(a) Ethylene Production by Pyrolysis of Ethane



(b) Ethylene Production with Simple Heat Recovery

Figure 4. Temperature (Kelvin) versus Enthalpy (10 x MJ/kmole) Diagrams for Ethylene Production

recovery would stop at point a, no more than 80% to 90% of the preheat required. The additional preheat must be provided by burning expensive high-quality fuel in the pyrolysis furnace.

As described by Kniel, et al (1980) a typical industrial pyrolysis system includes a pyrolysis furnace where the hydrocarbon feedstock is rapidly heated to c. 1100K followed by a so-called "quench cooler". The quench cooler is a steam-generating heat exchanger that typically produces steam at c. 125 bar. The product vapor is usually not cooled much below 400°C to avoid condensing heavy oils in the steam generator.

To illustrate the potential for process improvements and to allow an ecomonic and energy evaluation, simplified models of the conventional plant and a plant employing a BASE heat pump are needed. Straightforward measures are available for managing heat recovery at moderate temperatures and conventional practice avoids cooling of the products in the production unit itself to near ambient temperature. In addition, a BASE heat pump cannot operate at low temperatures. The plant models can be greatly simplified by considering only the higher temperature processes and assuming that lower temperature heat recovery and preheating are arranged for in conventional fashions.

In a simplified conventional plant the reactant gas, ethane, enters at 500K. In the pyrolysis furnace the ethane is heated to 1100K and decomposes into ethylene and hydrogen. The product then enters the quench cooler where steam is produced at 125 bar. Presuming the unit is part of a cogenerating bottoming cycle, electric work can be produced by the steam. Cooled product leaves the unit at 500K. Detailed calculations are outlined in Table 1.

The simplified plant for ethylene production using a high-temperature heat pump is illustrated in Figure 5. The reactant is preheated using the product gases as the source for a high-temperature heat pump. This is already a rather complicated system to analyze, so a computer program was written to couple the thermodynamics of the heat pump with the pyrolysis process. The crucial factor is the electric work required. Example results are shown in Table 2. For these results a BASE efficiency of 90% was assumed, also a temperature difference of 25 K° was assumed at both the evaporator and condenser. Note that disproportionately more work is required the greater the heat recovery because of the increasing temperature difference between the two streams.

Table 1

Ethylene Production in Pyrolysis Furnace
with Bottoming Cogeneration Cycle

reactant preheat (500K to 1100K)	63,517	kJ/(kmole)*
heat of reaction (at 1100K)	145,107	
heat input	208,624	
product heat recovery (to 500K)	68,180	
cogeneration cycle thermodynamic efficiency	22%	
boiler presure = 125 bar		
condenser pressure = 1 bar		
turbine efficiency = 0.9		
pump efficiency = 0.9		
generator efficiency	90%	
overall efficiency	20%	
fuel costs (natural gas)		
\$3.71/(1000 SCF)	\$3.41	/GJ
allow 85% furnace efficiency	\$4.01	/GJ
electricity costs		
\$.051/(kW hr)	\$14.17	/GJ
allow 50% as avoided cost	\$ 7.08	/GJ
cost summary:		
heat: (208,624kJ) (\$4.01/GJ) =	0.8366	
power: (68,180) (.20) (7.08) =	- 0.0965	
	\$0.7400	/km**

* All enthalpies are kJ per kmole of ethylene product.

** Cost per kmole of ethylene product.

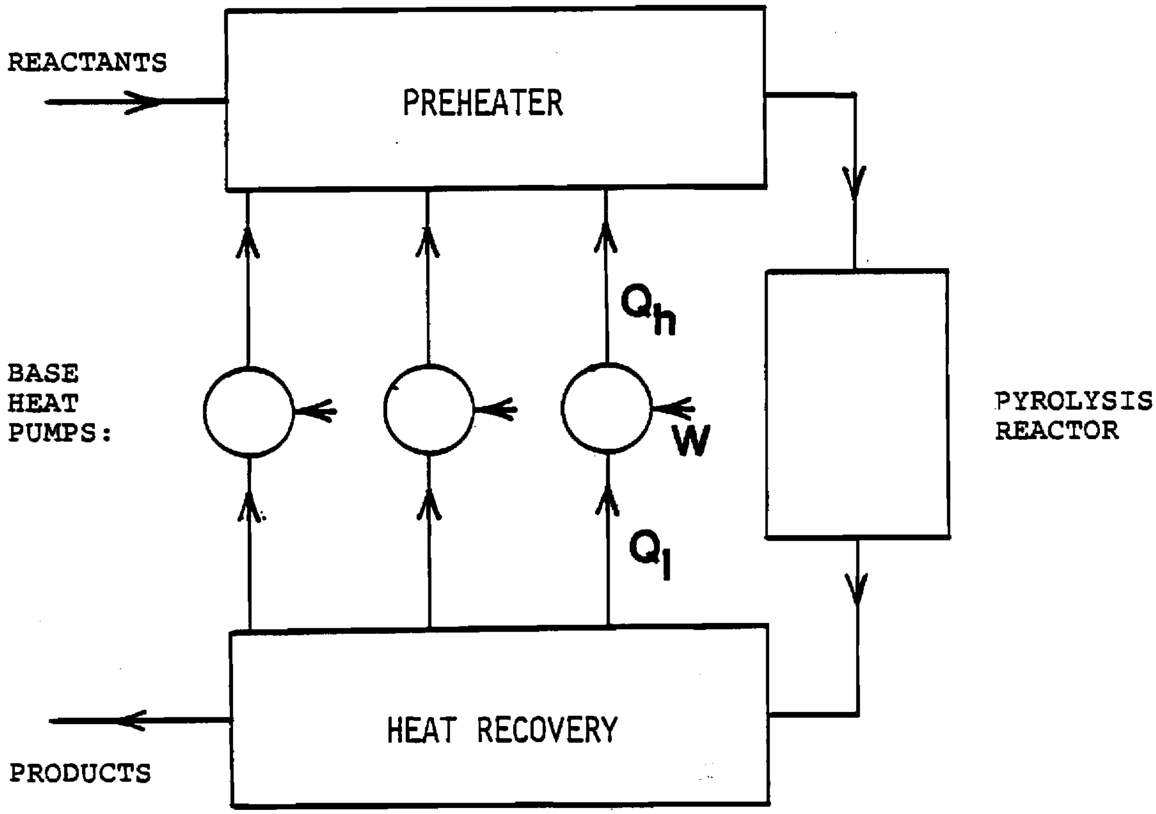


Figure 5. Schematic Simplified Plant for Ethylene Production Using High-Temperature Heat Pump

Table 2

Ethylene Production in Pyrolysis Furnace
with High-Temperature Heat Pump

	product outlet temperature 500K	550K	
reactant preheat and heat of reaction	121,167	140,529	kJ/km*
HTHP work input	19,277	4,598	kJ/km
fuel costs (natural gas)			
$3.71 /(1000 SCF)		$3.41	/GJ
allow 85% furnace efficiency		$4.01	/GJ
electricity costs			
$.051 / (kW hr)		$14.17	/GJ
allow 70% for interruptable serrvice		$9.92	/GJ

cost summary

	product outlet temperature 500K	550K	
fuel	.4859	.5635	
power	.1912	.0456	
	$.6771 /km	.6091	/km**

* All enthalpies are kJ per kmole of ethylene product.
** Cost per kmole of ethylene product.

Figure 1. A Representative Candidate Process for
a High-Temperature heat Pump
Application

The economic benefit of the alternative system is highly sensitive to the cost of electric power. The capital cost is expected to be somewhat lower with the BASE heat pump but the magnitude of any benefit here is uncertain. In the analyses shown in Tables 1 and 2, the national average costs for industrial users of fuel and power as reported by the U. S. Energy Information Administration (1985) are used. As is well known, the value of cogenerated power is controversial. For the purposes of analysis, the value of the electric work produced by the cogeneration cycle is assigned one-half the retail price as a measure of the true avoided cost. The cost of power to drive the BASE heat pump was assigned 70% of the average retail price as a potential inducement for a large user of interruptable power. The potential cost savings of 8.5% to 18% are very significant for this very cost-sensitive product.

The savings on a gross energy basis are even more marked. The production of one kmole of ethylene requires 245,440 kJ of fuel (heating value) in the conventional model but only 181,021 to 208,341 kJ using the heat pump process (assuming 29.39% efficiency for the electricity production). These savings are conservative as being based on conventional electricity production methods. As the technology for electricity-producing topping cycles such as high-temperature fuel cells and AMTEC's continues to advance, it will be possible to produce electricity for the cost of heat and provide the reject heat to high temperature uses such as the pyrolysis furnace.

As illustrated in this example potential benefits include energy savings, especially in processes involving high-temperature endothermic reactions, and other benefits such as:

1. Reduced thermal pollution and cooling water consumption in heat rejection.

2. Straightforward energy conservation avoiding the need for extensive plant integration which is expensive in construction, imposing on plant maintenance and operation, and inflexible to market demands and to the cost of competing fuels.

3. Allow for electrofication of processes that now require on-site burning. Expensive fuels can be displaced by cheaper coal and nuclear resources. Environmental degradation can be minimized by extensive abatement measures possible at the central utility facility.

1.1.3 Technical Feasibility and Impediments to Deployment

As illustrated in the previous calculations, a high-temperature heat pump employing BASE is thermodynamically feasible. While other thermodynamic cycles should be considered, the vapor-compression is the most promising candidate cycle and the reversed Ericsson cycle is a potential alternative. Certain technical questions remain. The effect of the contrary conduction of heat in the BASE on the performance of the vapor-compression cycle is crucial. Since the Ericsson cycle is rather more complicated requiring BASE components for compression and expansion as well as an internal recouperating heat exchanger, component efficiencies and effectiveness will have a marked effect on the performance of the system.

Some basic research, involving both theoretical and empirical investigations, on the transport of ions in non-isothermal BASE is warranted. A more detailed thermodynamic and transport model for the candidate systems will be required so that their performance can be assessed in potential applications. Such detailed performance results can be combined with costs analysis to determine the economical benefit of a BASE heat pump.

Certain external factors could inhibit the deployment of the BASE heat pump. At present, the production levels of petrochemicals may be stagnant. New capacity coming into operation may be in oil-producing countries where local fuel costs are arbitrarily low. This situation, especially in view of today's "oil glut", may discourage the construction of new plants that could use BASE heat pumps or the modification of existing plants.

An additional possible impediment may be rigidities in the detailed chemical processing. For example, ethylene is unstable at high temperatures. Consequently, in conventional processing, the hydrocarbon feedstock is rapidly heated and the product rapidly cooled or quenched. These very high heating rates may be incompatible with economical heat pumps.

1.1.4 Current Technology

The technology for energy-conversion devices employing BASE as heat engines (usually referred to as AMTEC, alkali-metal thermoelectric converters, or SHE, sodium heat engine, technologies) are well developed as outlined by Cole (1983) and Subramanian and Hunt (1983). The SHE might be deployed for nuclear power in space or as a topping cycle in coal-fired central electric plants, or modular-dish solar thermal power can exploit this technology.

The principal "competitor" to BASE heat pumps is the current pratice of thermal energy management in process synthesis and plant design. Ingenious methods including heat recovery, cogeneration, and reaction combination are features of today's highly integrated process plants. The BASE heat pump can be considered as an additional tool in plant integration. For example, a BASE heat pump can be used to overcome unfavorable temperature differences and facilitate high-temperature heat recovery. Alternatively, BASE may allow less well integrated plants to be energy efficient. This could save capital and allow more flexible response to the market demands.

1.2 Research and Development Needs

1.2.1 Immediate Needs

The most pressing needs are to demonstrate that BASE heat pumps are technically feasible and that economically advantageous applications exist. Preliminary research should address the following tasks:

1. Theoretical and empirical research on the transport of ions in non-isothermal BASE.
2. Development of thermodynamic and transport models for the BASE heat pump concepts.
3. Survey application in important sectors of the chemical process industries.
4. Develop projected cost and performance data and economic evaluations.
5. Present the results of work to the technical community.

1.2.2 Longer Term Need

Development of BASE heat pumps will not occur unless an organization with the requisite technical and financial resources undertakes a campaign of research, development, and demonstration. It is felt that if positive results are obtained from the preliminary research the foundation will be established to market this concept to capable firms. The important resources of the Georgia Tech Research Corporation and the Georgia Tech Advanced Technology Research Center are available to facilitate this activity.

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