



Process Heat for Chemical Industry

February 2021

Changing the World's Energy Future

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February 2021

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<http://www.inl.gov>

**Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

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Abstract (79 words)

Process heating with nuclear energy can reduce greenhouse gas emissions by reducing combustion of fossil fuels in fired heaters as steam boilers. Light water reactors can replace the majority of steam duties used by industry; however, high temperature processes such as steam methane reforming require advanced high temperature reactors. Guidance on matching the scale of nuclear reactors with specific industries is provided. Principles of heat transport, temperature boosting, and substitution for hot combustion gases are also discussed in this section.

Glossary

Exergy	The maximum theoretical useful heat and work (pressure-volume, shaft, or electrical) obtainable as the system is brought into complete thermodynamic equilibrium with the thermodynamic environment while the system reacts with this environment only
Microreactor	A nuclear reactor with a thermal energy output of ranging from one to 20 megawatt (MW) electrical energy generation
Small Modular Nuclear Reactors	A nuclear reactor with a thermal energy output of ranging from 20 to 300 megawatt (MW) electrical energy generation. Modules may be grouped to form a complex of reactors rivaling the output of traditional large-scale nuclear reactors (MSR).
High Temperature Gas Cooled Reactor	A nuclear reactor with a fuel core that is cooled by a gas, such as helium, nitrogen, or carbon dioxide (HGTR).
Molten Salt Reactor	A nuclear reactors with a fuel core that is cooled with a molten salt, such as eutectic mixtures of fluoride/lithium/beryllium (e.g., FLiBe) or sodium/potassium nitrate (e.g., NaNO ₃ -KNO ₃) or potassium/fluoride/zirconium (e.g. KF-ZrF ₄)
Brayton Cycle	A thermodynamic work cycle named after George Brayton that describes the workings a gas compression, gas heating and gas expansion turbine a gas cooling source, and gas compressor. paired to a heat source. A once-through air Brayton cycle draws and discharges air from the ambient atmosphere. A closed Brayton cycle incorporated a low-temperature heat rejection source.
Light water nuclear reactor	Nuclear reactor cooled by normal water (H ₂ O); either a pressurized water reactor (PWR) with steam generators that typically produces steam up to 330°C and 17.4 MPa or a boiler water reactor (BWR) that typically produces steam up to 290°C at 7.6 MPa
Subcritical Steam	Steam at conditions below the critical point of 374°C and 22.10 MPa
Supercritical Steam	Steam at conditions above the critical point of 374°C and 22.10 MPa
Ultra-Supercritical Steam	Steam at conditions which are typically greater than 600°C (and ranging up to 760°C) and in excess of 24 bar (and ranging up to 34 bar).
Next Generation Nuclear Plant	A concept for a project to provide nuclear energy to industrial processes; based on the high temperature gas-cooled reactor used for Next Generation Nuclear Plant (NGNP) concepts.

Key Words

Methanol
Greenhouse Gas Emissions
Combined Heat and Power
Advanced Reactors
Molten-Salt Reactor
High Temperature Gas-Cooled Reactors
Light-water reactors
Microreactors
Small Modular Nuclear Reactors (SMNRs)
Brayton Cycle
Steam Methane Reforming
Temperature Boosting
Exergy
Subcritical steam
Supercritical steam
Ultra-supercritical steam
Next Generation Nuclear Plant

Introduction

The Section Introduction (Chapter 0801, Bragg-Sitton and Boardman) discusses opportunities and gaps for application of nuclear produced thermal energy for the process industries. The most common methods of heat deposition in the process industry are performed with fired heaters that provide hot exhaust for gas-to-gas and gas-to-liquid heating, chemical reactor vessel jackets, steam reforming processes, and high temperature processes such as glass, cement, and steel making processes. It is estimated that about 70% of the energy supplied to the process industries is derived by combustion of fuels, including process tail gases that are conveniently burned to raise heat while avoiding pollutant emissions. It is therefore imperative that strategy intent on achieving deep decarbonization of industry look for a substitute for fossil fuel combustion. Moreover, it is important to note that unlike the transportation sector and electrical grid, energy use by industry often involves direct conversion of primary energy sources to thermal and electrical energy at the point of consumption. The heterogeneity and variations in scale of industry and the complexity of modern industrial firms' global supply chains are among the sector's unique challenges to minimizing its greenhouse gas (GHG) emissions. Because nuclear energy is essentially GHG-emissions free, concentrated, high quality, and wholly dispatchable, it is a strong candidate for providing process heat for the chemical industries.

This section necessarily begins with a review of best fit industries for initial application of nuclear-supported process heating. McMillan et al., (2016) composed the most complete review to date on process heating that can be supported by solar, geothermal, and nuclear energy sources. The diversity of processes within the industry represents many potential

applications for nuclear technologies. Many chemical processes have heat needs within the ranges generated by reactor designs (see Table 1 of the Chapter 0801, Introduction to Non-electric Applications).

Application of nuclear energy to industry is motivated by the same drivers as electrification of industrial manufacturing: reducing overall emissions from the industrial sector. However, the greatest thermodynamic efficiencies are ultimately attained by direct application of the thermal energy produced by nuclear reactors. This is borne out by understanding and applying a thermo-economic analysis. Application of the 1st and 2nd Laws of classical thermodynamics leads to an assessment of the disposition of the exergy input into the system. Exergy is the maximum theoretical useful heat and work (pressure-volume, shaft, or electrical) obtainable as the system is brought into complete thermodynamic equilibrium with the thermodynamic environment while the system reacts with this environment only (George Tsatsaronis, 1993). This necessitates a systematic analysis of both the work-producing (e.g., electrical power) and work-adsorbing processes (e.g., a gas liquefaction column or a chemical product reactor) unit operations.

Industrial Heat Requirements

Figure 1 shows the breakdown of emissions and the concentration and level of heat use by major industrial sectors. While the potash/soda ash/borate mining industry has relatively low total emissions and relatively few facilities over the reporting threshold, each plant consumes a large amount of thermal energy. Petroleum refineries account for the most emissions among considered industries, with many refineries in the U.S. consuming moderate levels of thermal energy.

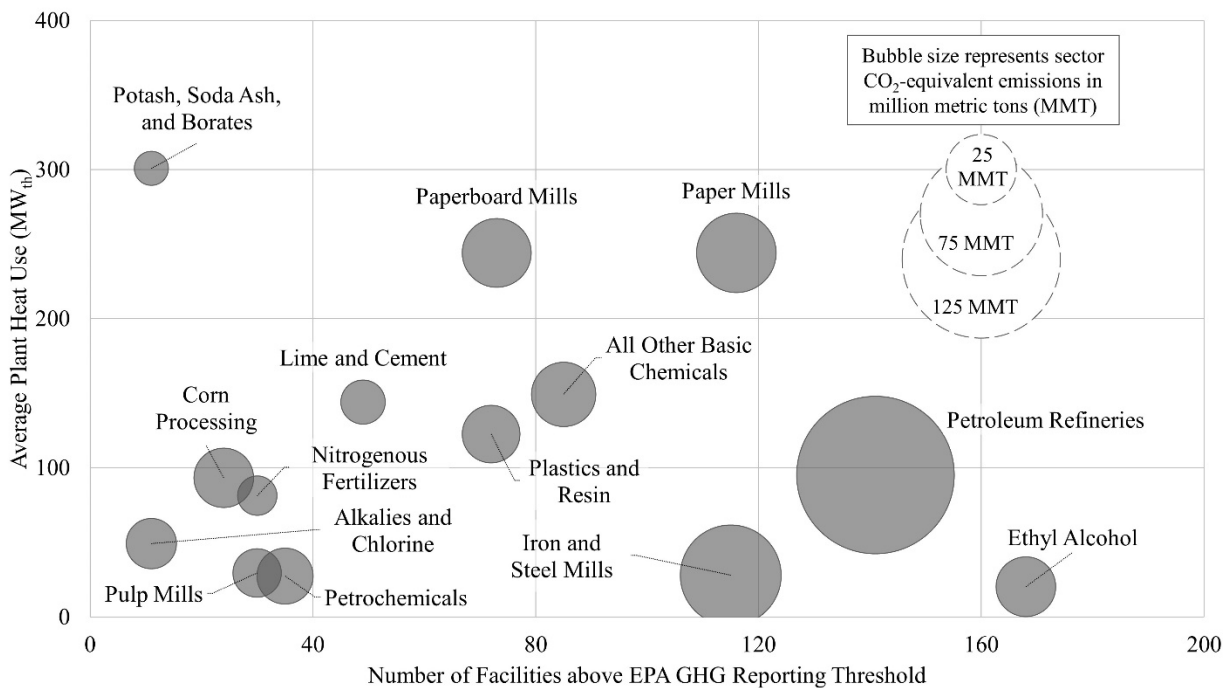


Figure 1: Size and emissions of selected industries in the U.S.

Approximately one-half of the heat used by industry is provided by package boilers to raise steam, which is the predominate medium of heat transport and heat transfer. Space heating accounts for about 20% of the total fuel usage, most of which is for boilers in houses.

The majority of steam duties simply require subcritical steam. Some applications may utilize supercritical steam, but it is rare for any process to use ultra-supercritical steam, except in power generation, given the corrosivity of high temperature steam which necessitates expensive alloys. For very high temperature processes, either direct or indirect heating with combustion gases is the most common practice. However, with the advent of advanced, high temperature reactors, it is desirable to substitute steam duties with non-corrosive hot gases. Inert gases such as He and CO₂, or even heated air, are some choices.

The common feature of all process industries is that they aim to convert raw materials into a new form by means of chemical and physical changes. Some of these “processes” are listed in Table 1. Most require external heat, some in very large quantities.

Table 1. Process Industry Examples of Processes Using Heat

Process Industry	Examples of Processes Using Heat
Petroleum Refining	Feedstock heating, distillation, hydrocarbon cracking, hydrocarbon reforming (i.e., steam-methane reforming)
Chemicals (includes ammonia, fertilizers, pharmaceuticals, alcohols, detergents, resins, polymers, textiles, paints/pigments/dyes)	Endothermic chemical reactions, hydrogenation, pyrolysis, distillation, purification, evaporation, crystallization, polymerization, drying, prilling
Metals Manufacture (includes iron, steel, copper, and other non-ferrous materials)	Smelting of ores, refining, alloying, melting, casting, forging, rolling, annealing, soaking and heat treatment, sintering
Nonmetallic Minerals and Acids (includes phosphorous, soda ash or caustic, sulfurous, chlorine, alkalis/alkaline)	Slurry concentration and drying
Refractories (includes bricks, pottery, glass, cement, and other refractory materials)	Firing, kilning, drying, calcining, melting, forming (e.g., plate glass), annealing
Wood Product (includes lumber, paper, and paperboard)	Kiln drying, wood pulping and liquefaction, rolling, drying, coating, and forming
Food and Drink (includes dairy products, brewing, farinaceous products, meat and vegetables, soft drinks, and tobacco)	Milling, blending, forming as liquids, powders, or composite solids, purification, sterilization, pasteurization, fermentation, refrigeration
Sugars and artificial sweeteners	Glucose-to-fructose conversion, artificial sweeteners
Industrial Gases	Temperature-swing adsorption

Nuclear Reactors for Process Heating

Nuclear heat is well-matched to process heating, and in some cases vaporizing chemical feedstock entering a reactor process. Nuclear heat can be directly substituted for steam that is used indirectly to dry, concentrate, or distill most aqueous solutions and to fractionate petroleum distillates. In some cases, nuclear heat can be used to break low-order chemical bonds such as biomass ligands or coal moieties. In summary, approximately 75% of all industrial

heat duties require less than 700°C, with about 50% of the duties being less than 300°C.

Figure 2 visualizes the temperature ranges of process heat required in selected industries described in Chapter 0801, Table 1 (Bragg-Sitton and Boardman, 2021) and compares to the output temperature limits of different nuclear reactor designs. As the figure indicates, advanced nuclear reactors (ARs) produce higher-quality heat than light-water reactors (LWRs), and therefore have a greater potential to replace existing industrial heat sources. Combined with an efficient, high-temperature heat transport system, such as solar industrial process heat systems used with solar concentrators, sodium fast reactors (SFRs), molten-salt reactors (MSRs), and high temperature gas-cooled reactors (HTGRs) are expected to be capable of supplying process heat for most processes in these industries without the need for topping heat. Where necessary, low-carbon heat augmentation can be supplied electrically or with chemical heat pumps (Bragg-Sitton et al., 2020). Also, use of advanced nuclear reactors in industries or plants with processes requiring lower-quality heat provide the opportunity for bottoming processes, such as electricity production. In light of these findings, and based on temperature compatibility alone, none of the industries in Figure 2 should be excluded from consideration for thermally coupled nuclear energy systems.

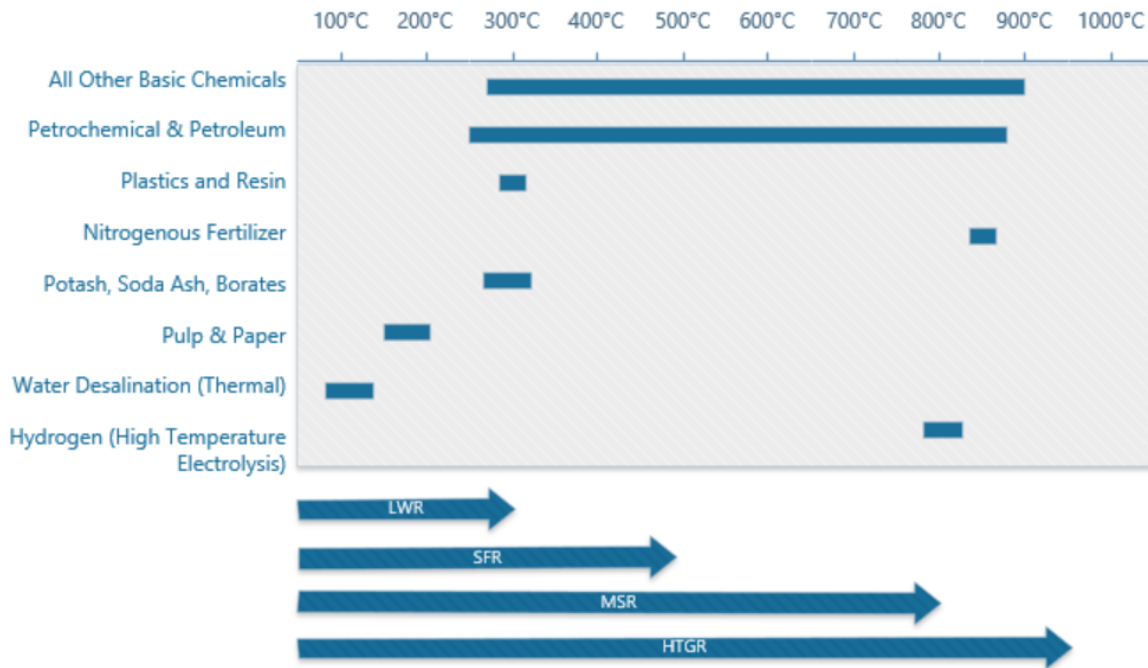


Figure 2: Comparison of industrial process heat ranges to output temperature limits of nuclear reactors. Sources: McMillan (2016) and MIT, (2018).

Naturally, a reactor’s thermal output capacity must exceed the thermal energy consumption requirements of the industrial plant or plants that it serves. Figure 3 shows the distribution of plant thermal energy consumption in four of the industries of interest. Plant size aligns well with the size of advanced reactors, which are expected to range from one to 20 MW_e for microreactors, 20 to 300 MW_e for small modular nuclear reactors (SMNRs), and from 300 to 1,000 MW_e and higher for full-size reactors. A breakdown of advanced reactors under development is given in a fact sheet by the United States Department of Energy (DOE 2020).

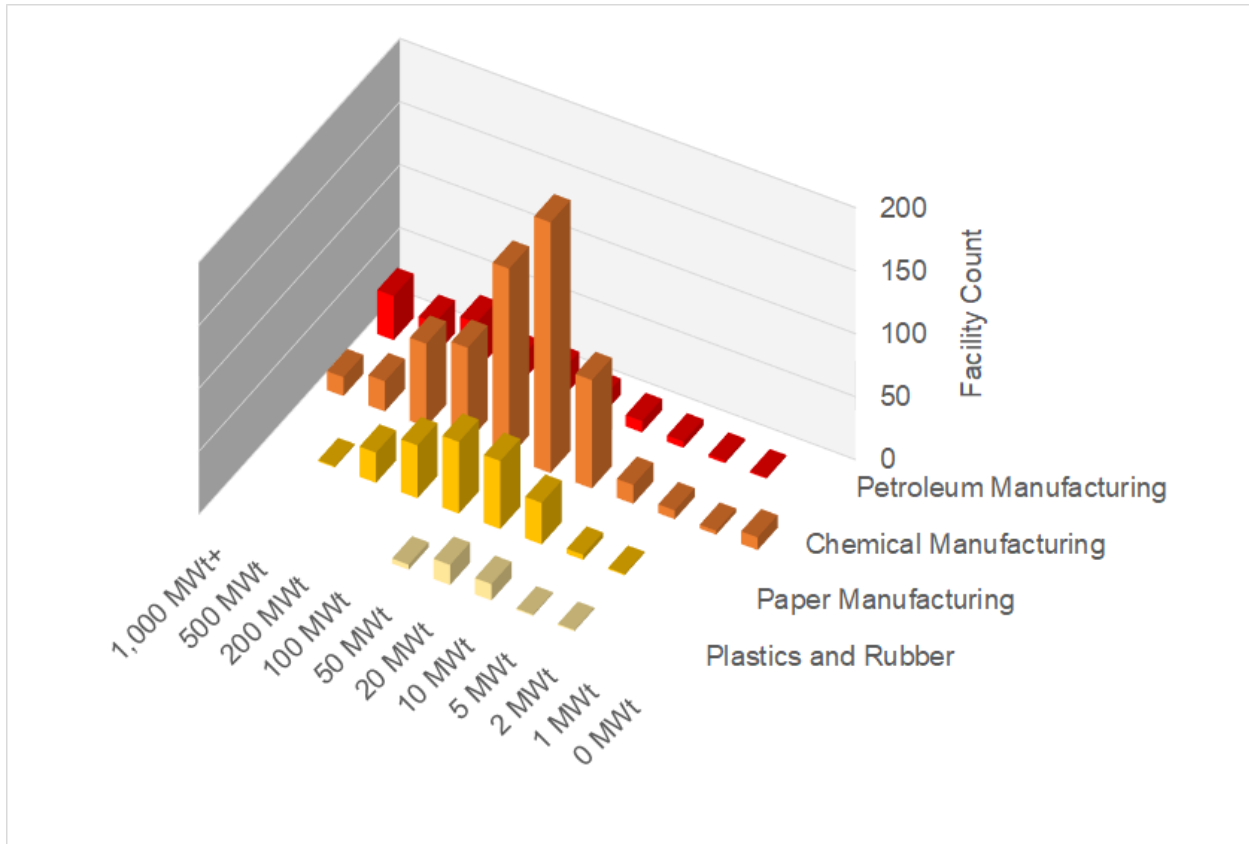


Figure 3. Distribution of plant heat consumption for different industries. Source: Analysis of EPA (2020)

Chemical Process Considerations (Subheading)

The main challenge for nuclear reactors is replacing fired-heaters that provide on-demand heating of chemical processes. The chemical process reactors, in which chemicals are made in industry, vary in size from a few liters to several cubic meters and hold, at any one time, well over 100 tonnes of materials. The design of the chemical reactor is determined by many factors, but of particular importance are the thermodynamics and kinetics of the chemical reactions being carried out.

In processes such as cement kilns, float glass making, and metals annealing, hydrocarbon-flames transfer heat by radiation to heat exchanger surfaces with the reactor vessel or process.

Cement kilns and metals decarbonization require very high temperatures that cannot be indirectly transferred to the solid. Hydrogen can be burned to provide very high temperature gases; however, hydrogen flames are virtually invisible and produce very little radiant heat to support indirect heating of a material.

The basic concepts for chemical process heating, evaporation, and reaction heating are illustrated in Figure 4. When evaluating the use of nuclear heat sources for the chemical industry, it is important to understand the chemical processes and the equipment used for feed heat-up, phase-changes, and reaction enthalpy requirements. Heat recuperation must be optimized in a manner that optimizes the use of the nuclear heat source. Finally, heat augmentation may be applied, but only when the net effect uses the energy contributed by the nuclear heat source (for example, see Figure 4(f)).

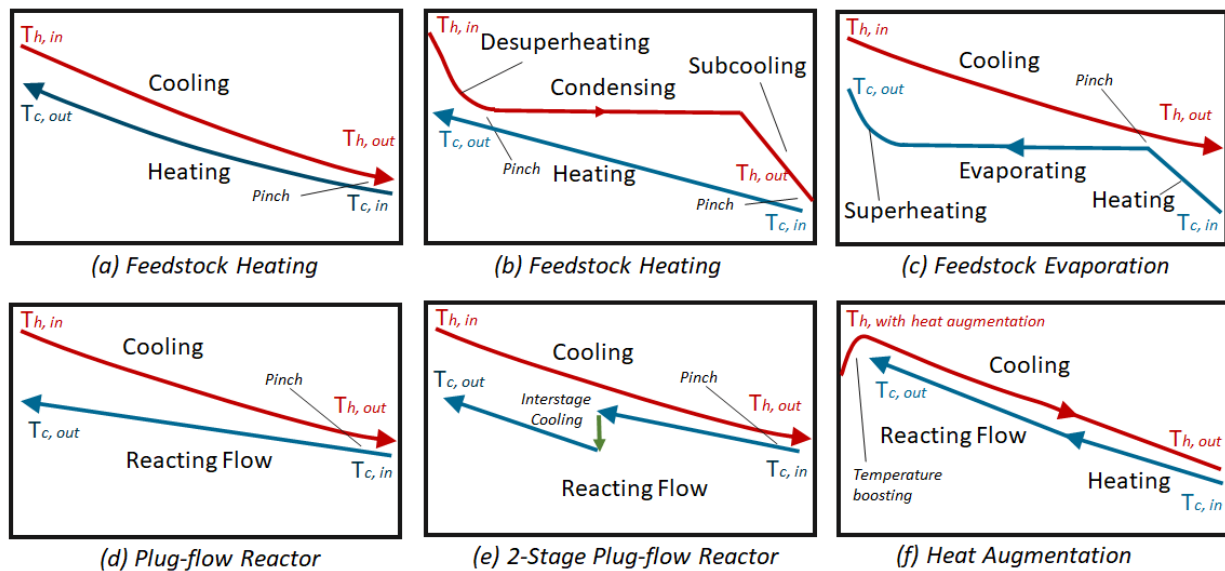


Figure 4. Nuclear heat transport to chemical process heaters and chemical reactors.

Fluid Mechanics Considerations (Subheading)

A number of integration issues must be considered when applying process heat applications to nuclear reactors. These considerations include:

- Reactor outlet temperature
- Reactor inlet temperature
- Fluid composition
- Pressure within coolant, heat transfer loop, and process heat application
- Tritium migration

Low temperature reactors—typically LWRs—can provide process heat to most industrial applications. Steam heating can be accomplished with topping heat from fossil fuels and/or electric resistance heating for higher temperature process heat applications. Conversely, high temperature heat produced by a high-temperature gas-cooled reactor (HTGR) or molten-salt reactor (MSR) may exceed the temperature limits of a given reaction process. In this case, a top-cycle use can be advantage, such a power generation unit. This is essentially the concept of a combined heat and power systems that converts supercritical pressure steam into power while dropping the pressure and temperature of the steam to the desired industry service quality. Similarly, a bottoming cycle may be necessary to lower the temperature of the heat transport media before its return to the nuclear heating loop.

In the case of the HTGR, the temperature difference of the gas temperature across the core optimally needs to be 350-450 °C. For most MSR concepts, the temperature difference is generally 50-150 °C, given the higher heat capacity of the salt versus a gas. In summary, the temperature of the thermal hydraulic heat delivery system must be carefully engineered. The choice of nuclear reactor depends on the industry heat application.

The melting temperature of liquid coolants, such as molten salts and sodium, and the heat transport system must be designed and operated to avoid freezing the salt. Depending on surrounding temperature, it may be necessary to insulate the pipes, pumps, and control valves of the delivery systems or to provide some form of electrical or jacket heating to re-liquify the frozen salt. Steam, carbon dioxide, and helium do not have such issues, although steam condensate traps and blow-out lines are needed at latitudes and altitudes where temperature may drop below the freezing point. For this reason, synthetic oils have become a preferred heat delivery media.

Heat transfer distance and the working fluid can both be limiting factors when considering industrial process heat input requirements. In the case of an application similar to the following artist's rendition (Figure 5), coupling between the nuclear reactor and one or more industrial processes may involve a heat transport distance less than 1 kilometer. As this distance expands, the choice of heat transport media and thermal energy circulation loop become more important. The tradeoff between liquid pumping and gas compression costs may alone determine the choice of heat transfer media.

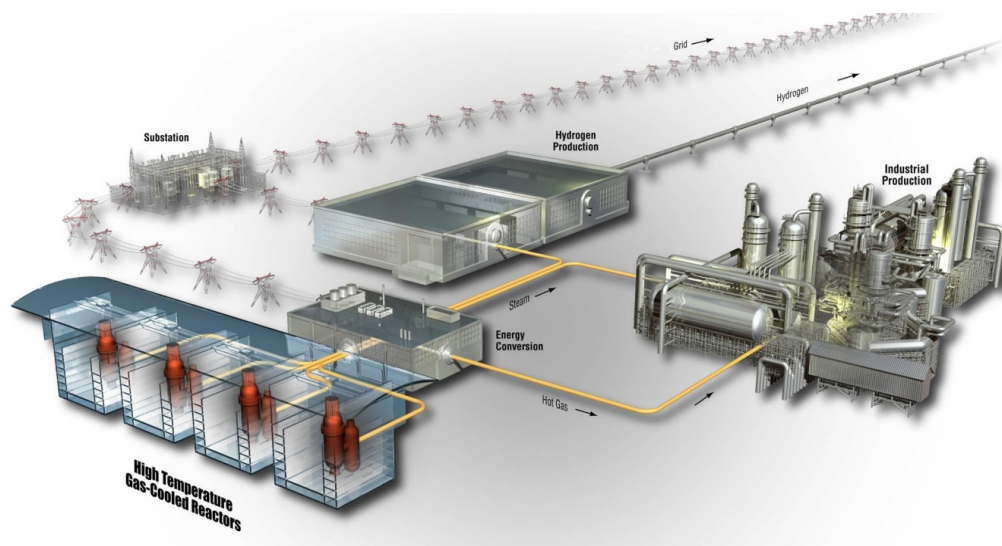
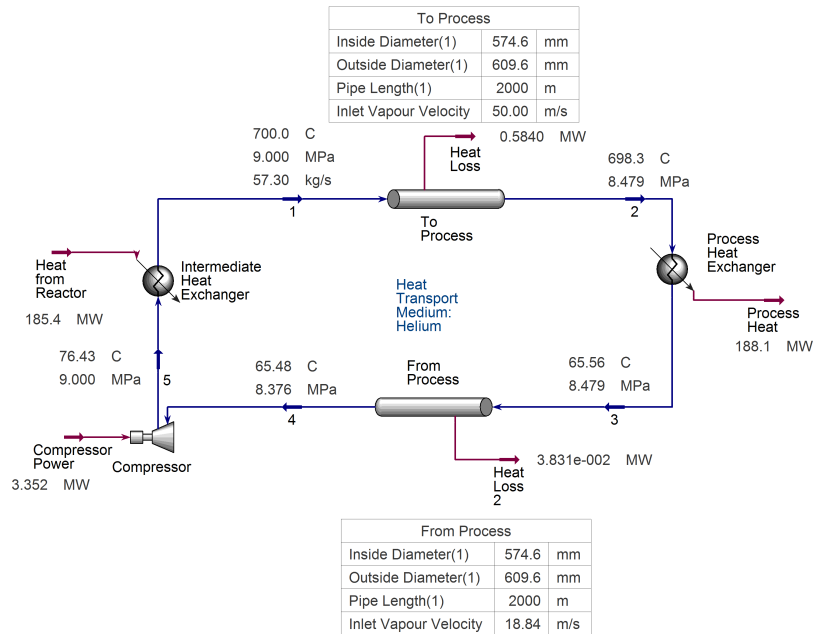


Figure 5. Artist rendering of the High Temperature Gas-Cooled Reactor to industrial plants
 Source: Next Generation Nuclear Plant Alliance (Nelson et al., 2011).

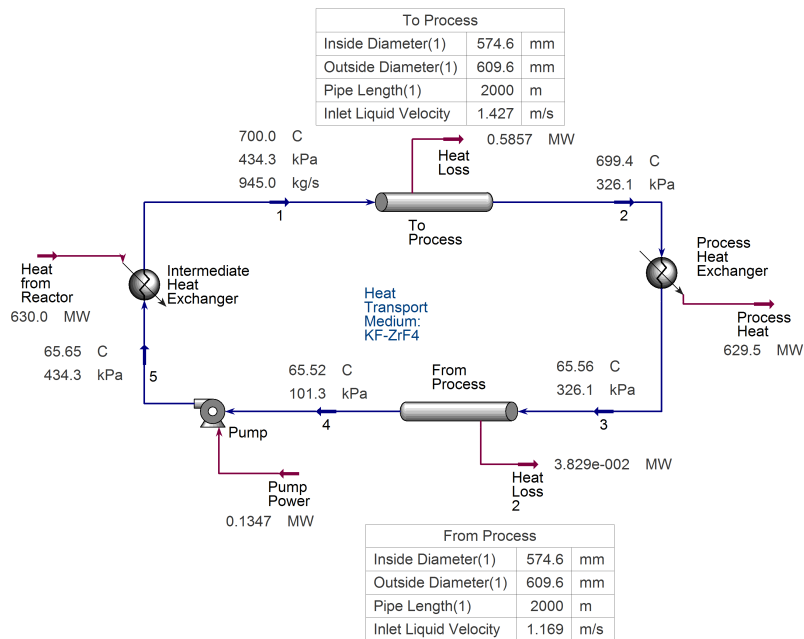
Long Heat Transport Distances (Subheading)

Engineering considerations for heat-transfer distance, such as capacity matching and working fluid temperature, are straight forward, but not necessarily easy. Steam/water and molten salts perform better than gases for relatively long heat-transfer distances (up to 20 km), primarily because gases such as helium require extremely high pumping power (McKellar 2011). The high pumping power makes long-distance hot-gas heat transport applications impractical (Yoon and Sabharwall, 2014; McKellar et al. 2011).

Figure 6a and 6b compares the transport of molten KFZrF_4 to helium using a circulation loop of a comparable size. For this comparison, the pipe is considered to be buried, although this may not be practical when considering thermal-expansion design requirements. The molten salt, having the highest volumetric heat capacity and lowest pumping energy, is capable of transporting 54.4 TJ/day or 629 MW_t (at a coefficient of performance of 4,670 TJ/day- MW_e) versus 16.3 TJ/day or 188 MW_t (at a coefficient of performance of 4.85 TJ/day- MW_e) using helium in the same sized piping system. The coefficient of performance is the heat divided by the pumping or compression power used to transport the heat. In a practical engineering design, pipe material and corrosion, as well as pump versus compressor costs, are important considerations.



(a) 2-km helium circulation loop, where the dimensions for pipe section 1 are tabulated



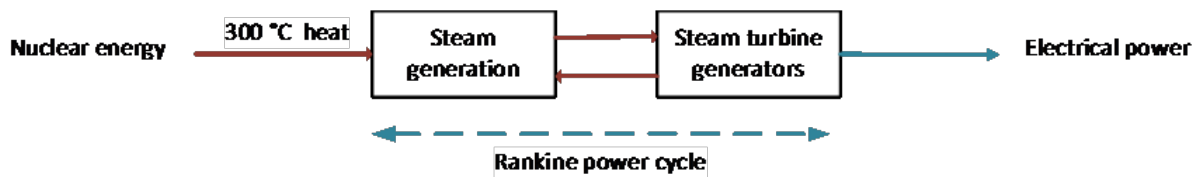
(b) 2-km KFZrF4 molten-salt circulation loop, where the dimensions for pipe section 1 are tabulated

Figure 6. Operating conditions and performance of high temperature reactor heat transfer loops (McMillan et al, 2016)

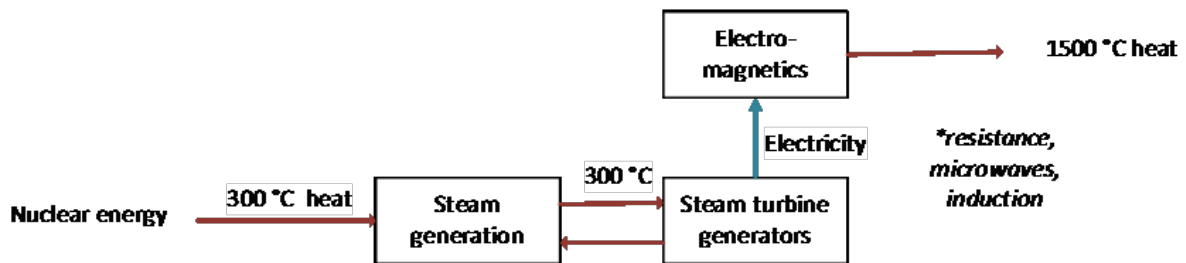
Process heat applications generally require a secondary heat transfer loop to isolate the primary core cooling loop from the process heat application. One purpose of this secondary loop is to reduce the migration of tritium from the reactor core to the process product. Additional heat transfer loops may be added to reduce tritium migration, but each loop degrades the exergy of the process heat temperature.

Temperature Boosting (Subheating)

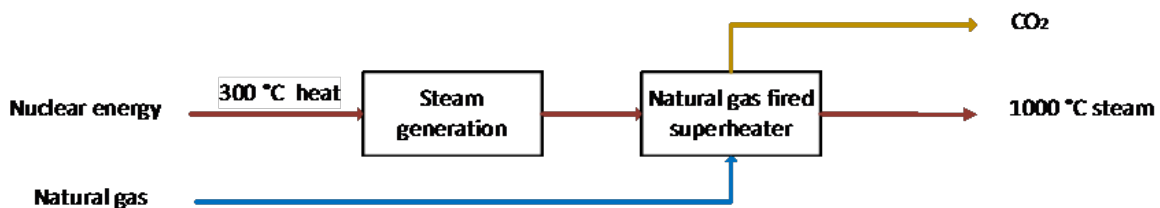
Temperature boosting through heat pumping is one approach to use energy conversion processes to create high temperature heat from the relatively low temperature heat produced by LWRs. There are a variety of possibilities for these conversions; some of which are illustrated in Figures 7(a)–(e). Thermodynamic principles require a net input of work to raise the temperature of heat in this manner, with more work needed as the final temperature increases. If an LWR provides the work input, the net effect is to convert a given amount of its 300 °C heat into a somewhat smaller amount of high temperature heat. However, this high temperature heat comes from a CO₂-free non-combustion source, providing environmental benefit relative to most current industrial practices. Table 2 compares other factors specific to each of these cycles. A variety of chemical looping possibilities have been developed. An exergoeconomic analysis is required to justify any application of these concepts.



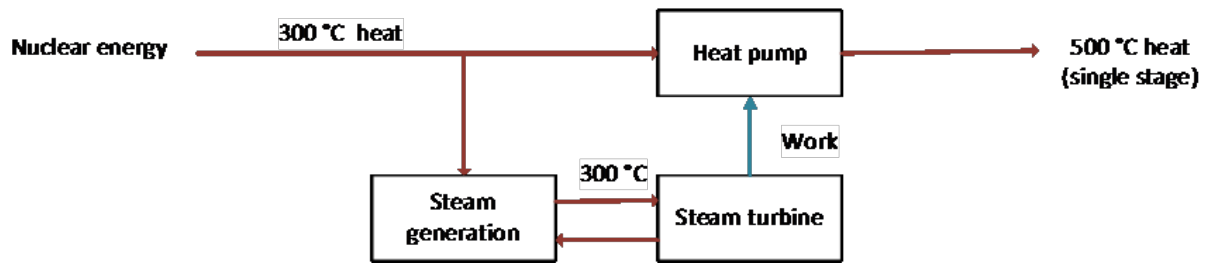
(a) Conventional power production



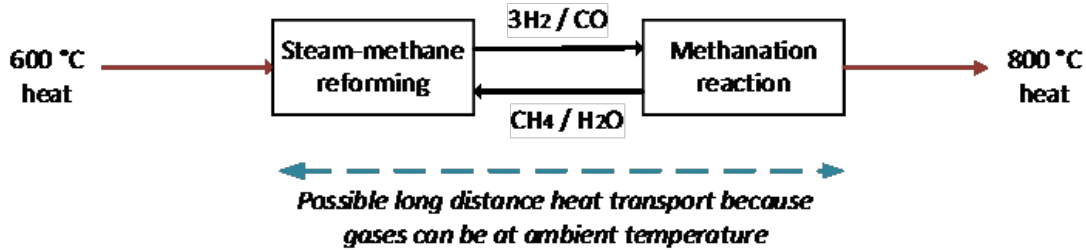
(b) Use of electric power to generate heat



(c) Fossil-fired topping cycle with nuclear heat



(d) Split-duty heat pump



(e) Looping chemical reaction

Figure 7. Temperature boosting heat pump concepts

Table 2 Comparison of Energy Conversion Cycles for Making High Temperature Heat

Process	Delivery temp. range	Heat delivery efficiency	Advantages	Disadvantages	Comment
Rankine cycle	Makes power	32-34% as power	Well established technology	Makes power, not heat Fairly low efficiency	Reference process
Electric-based heating	To melting point of materials, 1500 °C	33% to power, 100% power to heat	Well established technologies Easy to integrate into applications	Fairly low efficiency No particular synergy with nuclear generation	Isothermal heat delivery
Fossil-fired topping	To melting point of materials, 1500 °C	~85% for furnace	Well established technology	Half or more of heat input comes from the furnace Associated CO ₂ emissions	Energy delivered as sensible heat over a temperature range
Split duty heat pump	ca. 200 °C increase per stage	~60% per stage, rest is reject heat	All energy comes from the nuclear reactor Adaptable for cogeneration	High temperature compressors are not standard items (but turbines are)	Explore working fluids besides steam

			Only a small amount of equipment sees high temperatures		
Chemical reaction for heat delivery	ca. 800 °C, perhaps to 1000 °C	Estimated 60-70%	Can support long distance heat delivery by piping cold gas Storage of energy (as syngas mixture) is possible Could integrate with a HTGR	Requires intermediate temperature heat input for reforming (could potentially integrate with a heat pump)	Explore other endothermic chemistry, such as water splitting Heat can be delivered roughly isothermally

Example: Use of Nuclear Heat for Methanol Production

Methanol is one of the predominant commodity chemicals in the United States and around the world. It is a feedstock to produce chemicals, such as acetic acid and formaldehyde, which in turn are used in products such as adhesives, foams, plywood subfloors, solvents, and windshield washer fluid. In recent years, the use of methanol in the production of olefins, or methanol-to-olefins, has grown rapidly (Alvarado 2016). Methanol can also be used on its own as a vehicle fuel or blended directly into gasoline to produce a high-octane, efficient fuel with lower emissions than conventional gasoline.

There are at least two opportunities to replace natural gas combustion in methanol production: one is the heat needed for the primary reformer, and the second is the heat required for methanol purification. The former case is illustrated Figure 8. In conventional steam reforming, methane is reformed in tubes within a furnace. Heat is provided by firing natural gas. Heat transfer from the flame to the tubes is primarily via thermal radiation.

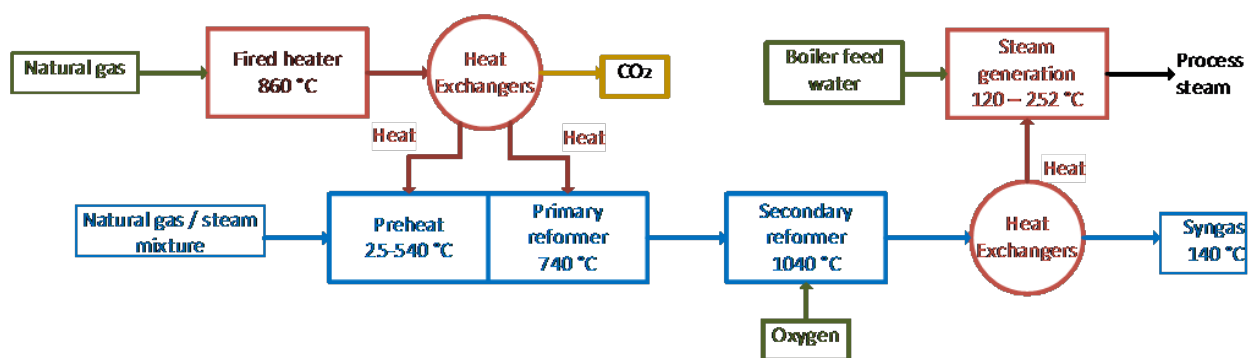


Figure 8. Energy use in synthetic gasoline production for use in methanol synthesis

When heat is available above 700°C (i.e., high temperature molten-salt or gas-cooled reactors), it is possible to integrate nuclear heat directly into the natural gas reforming process, thus displacing combustion of natural gas as the primary source of reforming heat. A brief

discussion of heat integration for the various scenarios is presented below.

Figure 9 shows a simple block flow diagram indicating heat delivery to the primary reformer in a natural gas reforming plant (Wood and McKellar 2013). In this example, the primary coolant for a fluoride/lithium/beryllium (FLiBe) high temperature reactor (FHR) is used to heat helium, which is then pumped into the primary natural gas reforming heating box. The hot helium replaces the hot gas produced by natural gas combustion, which in some reforming plants consumes as much as 30% of the natural gas input to the plant. The helium loop also provides separation of the primary reactor coolant from the chemical plant.

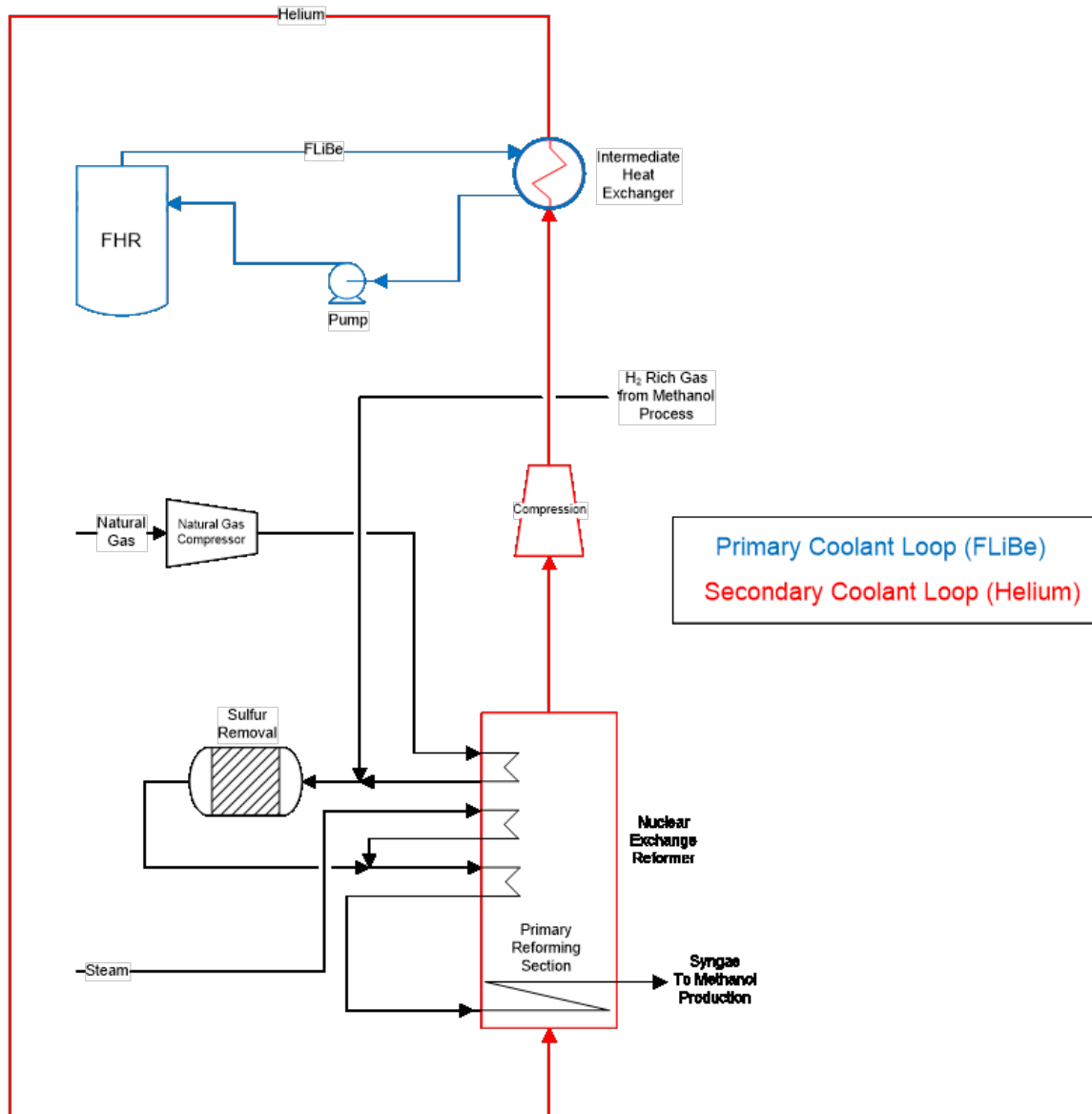


Figure 9. Steam methane reforming with a fluoride-salt high temperature reactor (FHR)

Bragg-Sitton et al., (2013) evaluated the technical and economic feasibility of producing methanol using a hybrid system in which the FLiBe salt is circulated in two parallel loops (Figure

10): (1) a primary loop that exchanges heat with a helium heat transfer loop to deliver heat to a methanol plant in the manner described above, and (2) a secondary high temperature heat transfer loop fluid that uses molten KF-ZrF_4 salt to transfer heat to a supercritical CO_2 Brayton Cycle power generation plant. The pressure of the helium loop was set at 9 MPa.

The methanol process generates some excess steam that is fed to a small Rankine cycle. The amount of power generated from this cycle, however, is insufficient to meet the entire electrical duty of the plant. The Brayton cycle therefore supplies power to the methanol plant to avoid the need for the methanol plant to import power from the grid. Excess power can be sent to the grid—an action that can be desired to support grid demand.

A discussion of the economics for the hybrid methanol and electrical power case is presented by Bragg-Sitton et al. (2013). For this case study, a dynamic model was developed to evaluate the profitability (measured in terms of the net present value of the project) as a function of variable energy apportionment between the power cycle and the chemical plant. The study developed a physics-based transient process model to simulate dynamic ramping of the natural gas reforming and power generation blocks in accordance with grid demands tied to wind power variation and grid supply demands. This type of hybrid system results in underutilization of the capital assets while optimizing profit by responding to the highest value market. For this case study, a positive profitability of this example hybrid system was achieved when wind penetration exceeds 20% of total system capacity. This was attributed to the high value of electricity when reserve capacity is required.

Additionally, at approximately this level of variable power generation capacity, traditionally baseload plants begin to be affected and are required to flex their operations. The benefits of an integrated plant, and similar hybrid systems, depends on the local grid markets, the chemical commodities markets, and the stochastics of variable power generation sources.

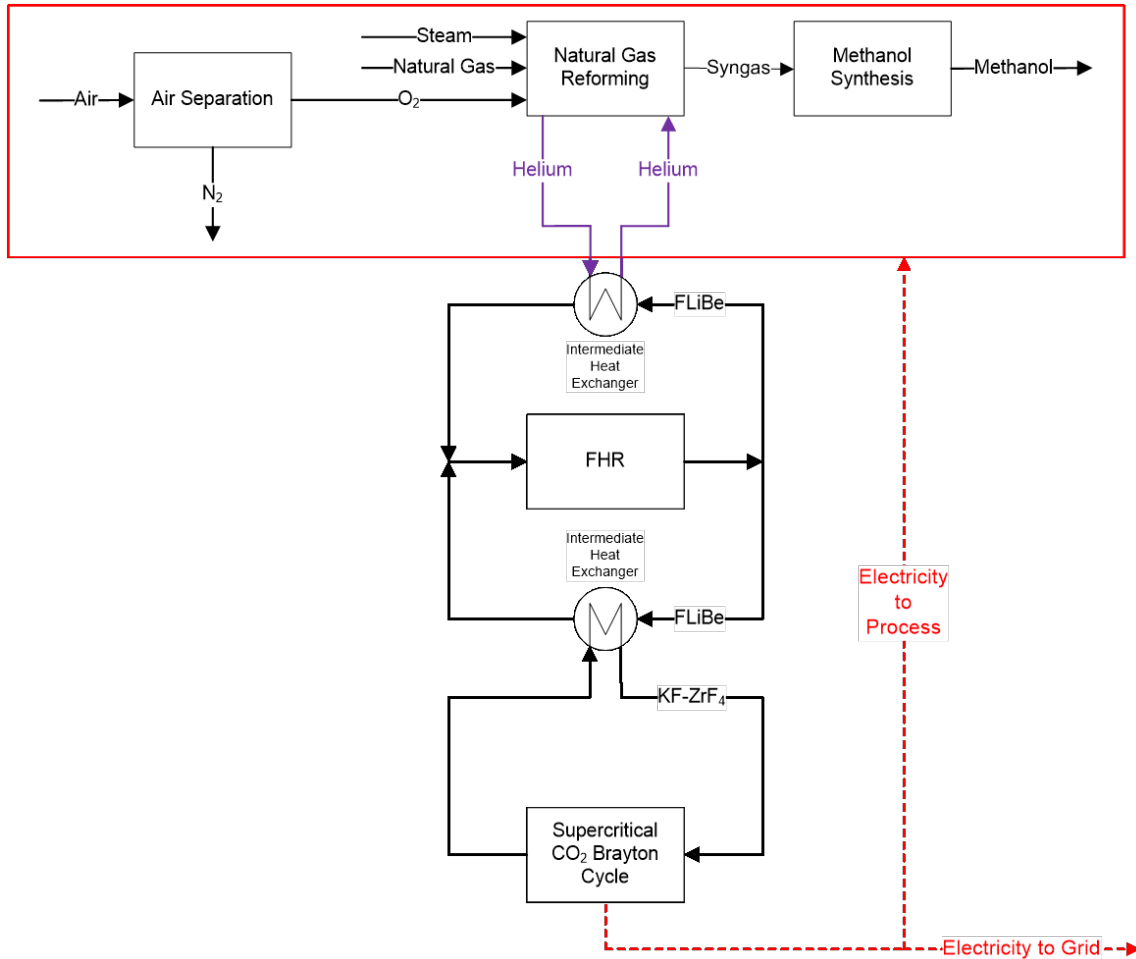


Figure 10. Advanced hybrid FHR methanol configuration.

Conclusions

This section highlights the opportunity to use nuclear heat for a wide spectrum of industrial manufacturing processes. This could arguably reduce industry GHG emissions by 90% when eliminating combustion in steam boilers, combined heat and power systems, fired-heater, and high temperature processes. The application of nuclear heat may be as simple as supplementing or replacing the steam duties of a plant to direct heat transfer to a chemical reaction process vessel. The cost of nuclear depends on many factors, but the impetus to reduce climate altering gases like CO₂ provides motivation to the nuclear heat sources. There remains a significant amount of research to understand the optimum choice of nuclear reactor to use and the separation between tightly coupled systems. However, the studies that are being completed in this area, including the limited examples shown in the Chapter, are promising. Dynamic operation of integrated energy systems is especially of high interest because these systems can help firm the grid when the penetration of variable generation sources like wind and solar energy begins to affect traditional baseload plant operations.

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