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IMECE 2011

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November 2011

The INL is a
U.S. Department of Energy
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IMECE2011-62588

LIQUID BIO-FUEL PRODUCTION FROM NON-FOOD BIOMASS VIA HIGH TEMPERATURE STEAM ELECTROLYSIS

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ABSTRACT

Two hybrid energy processes that enable production of synthetic liquid fuels that are compatible with the existing conventional liquid transportation fuels infrastructure are presented. Using biomass as a renewable carbon source, and supplemental hydrogen from high-temperature steam electrolysis (HTSE), these two hybrid energy processes have the potential to provide a significant alternative petroleum source that could reduce US dependence on imported oil. The first process discusses a hydrolysis unit with hydrogen addition from HTSE. The second process discusses a process named Bio-Syntrolysis. The Bio-Syntrolysis process combines hydrogen from HTSE with CO from an oxygen-blown biomass gasifier that yields syngas to be used as a feedstock for synthesis of liquid transportation fuels via a Fischer-Tropsch process. Conversion of syngas to liquid hydrocarbon fuels, using a biomass-based carbon source, expands the application of renewable energy beyond the grid to include transportation fuels. It can also contribute to grid stability associated with non-dispatchable power generation. The use of supplemental hydrogen from HTSE enables greater than 90% utilization of the biomass carbon content which is about 2.5 times higher than carbon utilization associated with traditional cellulosic ethanol production. If the electrical power source needed for HTSE is based on nuclear or renewable energy, the process is carbon neutral. INL has demonstrated improved biomass processing prior to gasification. Recyclable biomass in the form of crop residue or energy crops would serve as the feedstock for this process. A process model of syngas production using high temperature electrolysis and biomass gasification is presented. Process heat from the biomass gasifier is used to heat steam for the hydrogen production via the high temperature steam electrolysis process. Oxygen produced from the electrolysis process is used to control the oxidation rate in the oxygen-blown biomass gasifier.

INTRODUCTION

Nuclear energy can contribute to energy security in the volatile transportation sector in several ways. In the near term, nuclear energy can be used for hydrogen production to support refining of increasingly lower quality petroleum resources such as oil sands and heavy crudes. In the longer term, supplemental hydrogen will be required for synthetic liquid fuels production based on coal or biomass. Traditional processes for producing liquid fuels from biomass or coal are very carbon inefficient, with a high percentage of the feedstock carbon emitted as carbon dioxide during fuel synthesis. The use of supplemental nuclear hydrogen can increase carbon utilization to 95% or higher, with no additional carbon emissions. In the long term, nuclear hydrogen can also be used as a direct vehicle fuel in hydrogen fuel cell vehicles (HFCV). Nuclear energy can also contribute directly to the transportation sector by supplying carbon-free electric power for recharging battery-electric vehicles (BEV). Analysis has shown that all US light-duty vehicle miles could be powered by 130 GW of supplemental power generation, assuming that the light-duty fleet consists of HFCV/BEVs that have 40 mile electric range and that the hydrogen needed for extended range in HFCV mode is generating using high-temperature electrolysis [1].

At present, hydrogen production in North America is based almost exclusively on steam reforming of methane. From a long-term perspective, methane reforming may not be sustainable for large-scale hydrogen production since natural gas is a non-renewable resource that exhibits large volatility in price and since methane reforming and other fossil-fuel conversion processes emit large quantities of greenhouse gases to the environment [2]. Non-fossil carbon-free options for hydrogen production include conventional water electrolysis coupled to either renewable (e.g., wind) energy sources or nuclear energy. The renewable-hydrogen option may be viable as a supplementary source, but would be very expensive as a

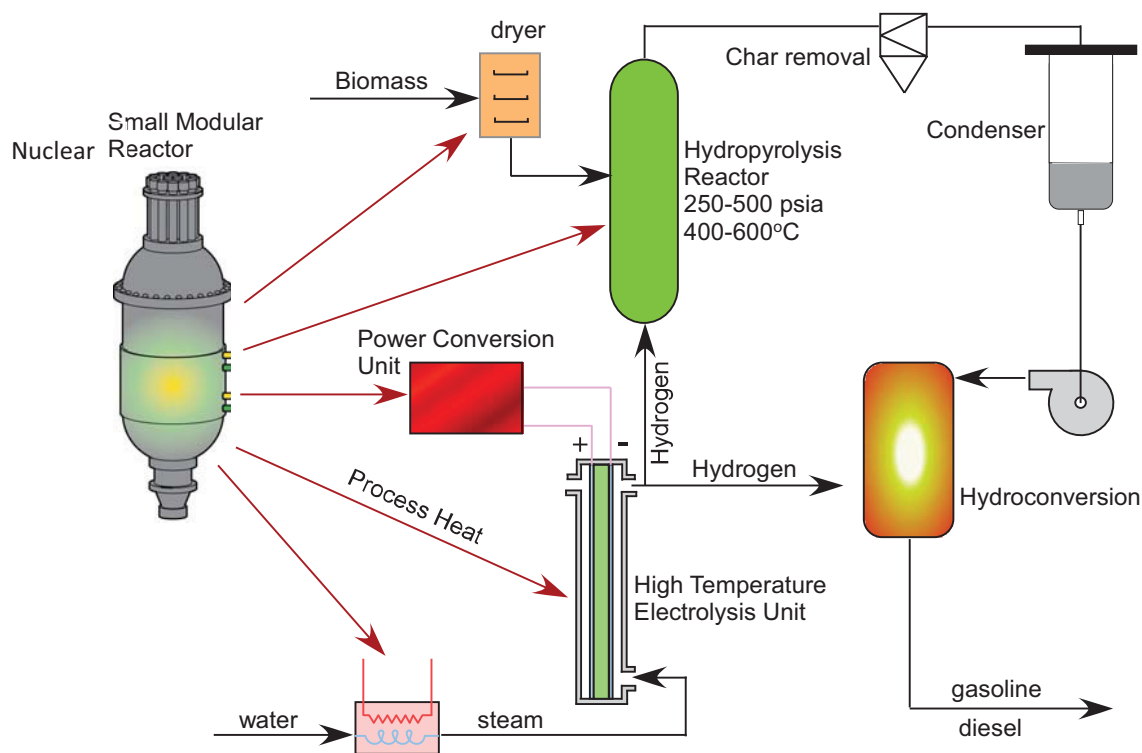


Figure 1. Hydropyrolysis for nuclear powered biomass-to-liquids with supplemental hydrogen from HTSE.

large-scale stand-alone option [3]. Conventional electrolysis coupled to nuclear base-load power can approach economical viability when combined with off-peak power, but the capital cost is high [4]. To achieve higher overall hydrogen production efficiencies, high-temperature steam electrolysis (HTSE) [5] can be used. High-temperature nuclear reactors have the potential for substantially increasing the efficiency of hydrogen production from water, with no consumption of fossil fuels, no production of greenhouse gases, and no other forms of air pollution.

Small modular reactors (SMRs) can potentially be used to power hybrid energy systems that enable production of synthetic liquid fuels that are compatible with the existing conventional liquid transportation fuels infrastructure. Using biomass as a renewable carbon source, and supplemental hydrogen from high-temperature steam electrolysis (HTSE), these systems have the potential to provide a significant alternative petroleum source that could reduce US dependence on imported oil. Combining hydrogen from HTSE with CO from an oxygen-blown biomass gasifier yields syngas to be used as a feedstock for synthesis of liquid transportation fuels via a Fischer-Tropsch process. Conversion of syngas to liquid hydrocarbon fuels, using a biomass-based carbon source, expands the application of nuclear and renewable energy beyond the grid to include transportation fuels. It can also contribute to grid stability associated with non-dispatchable power generation. The use of supplemental hydrogen from HTSE enables greater than 95% utilization of the biomass carbon content which is about 2.5 times higher than carbon

utilization associated with traditional cellulosic ethanol production. If the electrical power source needed for HTSE is based on nuclear or renewable energy, the process is carbon neutral. INL has demonstrated improved biomass processing prior to gasification [6]. Recyclable biomass in the form of crop residue or energy crops would serve as the feedstock for this process.

The safety aspect of the proposed process is too much to discuss in this paper. A typical nuclear power plant costs between \$2-4 billion per GW of electrical power. Revenue would not be generated for a long period of time.

PROCESS DESCRIPTIONS

Hydropyrolysis: A schematic of a hydropyrolysis process is provided in Fig. 1. The process is directly coupled to a small modular reactor for both process heat and power. The process heat demands are depicted in the schematic. This hydropyrolysis process injects high temperature hydrogen into the pyrolyzer with a fluidized bed catalyst that reacts with the biomass. The hydrogen upgrades the bio-oil that forms in the pyrolyzer. The additional hydrogen reacts with the oxygen in the biomass and forms water, thus allowing the remaining biomass with the basic chemical formula of CH_2 to form a nice synthetic fuel. Char is produced in the hydropyrolysis process and is taken out after the pyrolyzer and is a valuable commodity, especially if carbon credits are available. Additional treatment of the fuel occurs in the hydro conversion unit where another catalyst removes the remaining oxygen.

This process is similar to the GTI process described in Ref [7]. GTI does not disclose the material or nature of the catalysts used.

The process heat demands include a steam generator, a high temperature steam electrolysis unit, a power conversion unit (PCU), a hydrolysis reactor, and a biomass dryer. The steam generator produces steam for feed to the high temperature steam electrolysis unit. For highest efficiency operation, the HTSE unit operates in a net endothermic mode, requiring a net high temperature process heat input. A more complete description of the high temperature electrolysis process is given below. Nuclear process heat is also required for power generation via the power conversion unit (e.g., Rankine cycle). Depending on the plant configuration, the SMR and the PCU could be sized for dedicated biomass-to-liquids (BTL) operation. Alternately, the reactor and PCU could be sized for excess power generation, beyond what is required for liquids fuels production. Power supplied to BTL or to the grid could be varied daily and seasonally to maximize profit. The reactor also supplies process heat to the hydrolysis unit, which operates endothermically. The range of operating pressures and temperatures for the hydrolysis unit is indicated in Fig. 1. Finally, reactor process heat is supplied to the biomass dryer to remove excess moisture from the carbon feedstock. This heating could possibly be supplied at lower temperature, using heat rejection from the power cycle. It should be noted that a fully developed process would include as much heat recuperation from the various processes as is feasible to minimize the overall net high temperature heat requirement.

High Temperature Electrolysis. The biomass-to-liquids synthetic fuels production processes described in this paper require supplemental hydrogen for efficient conversion of biomass to liquid hydrocarbon fuels. Supplementary hydrogen is used in conventional refining processes for hydrocracking and hydrogenation of increasingly low quality petroleum resources. The supplementary hydrogen used in conventional refineries is produced almost exclusively from steam reforming of methane, a process that increases the already high demand for natural gas while emitting significant quantities of carbon dioxide into the atmosphere. High temperature electrolysis offers an efficient carbon-free alternate route to hydrogen production. In fact, HTSE has the highest conversion efficiency of any water splitting process that is driven by electricity. HTSE is based on electrochemical splitting of steam into hydrogen and oxygen. High temperature electrolysis makes use of solid-oxide cells, similar to solid oxide fuel cells, but operating in reverse with a per-cell operating voltage greater than the open-cell voltage. High-temperature electrolytic water-splitting supported by nuclear process heat and electricity has the potential to produce hydrogen with overall thermal-to-hydrogen efficiencies of 50% or higher, based on high heating value. From 2003 – 2009, development and demonstration of advanced nuclear hydrogen technologies were supported by the US Department of Energy under the Nuclear Hydrogen Initiative [8] during 2009, which sponsored

a technology down-selection activity in which an independent review team recommended high temperature electrolysis (HTE) as the most appropriate advanced nuclear hydrogen production technology for near-term deployment [9].

The INL HTE program also includes an investigation of the feasibility of direct syngas production by simultaneous electrolytic reduction of steam and carbon dioxide (coelectrolysis) at high temperature using solid-oxide cells. Syngas, a mixture of hydrogen and carbon monoxide, can be used for the production of synthetic liquid fuels via Fischer-Tropsch or other synthesis processes. This concept, coupled with nuclear energy, provides a possible path to reduced greenhouse gas emissions and increased energy independence, without the major infrastructure shift that would be required for a purely hydrogen-based transportation system [10]. Furthermore, if the carbon dioxide feedstock is obtained from biomass, the entire concept would be climate-neutral.

As an alternative to centralized large-scale systems with direct coupling to high-temperature reactors, distributed hydrogen production could be accomplished using modular HTE units powered from grid electricity and an alternate high-temperature heat source such as concentrated solar energy [11] or a biomass gasifier [12]. This approach could be quite economical if off-peak electricity is used [13].

To demonstrate the performance potential of advanced nuclear hydrogen systems, detailed process analyses have been performed [14]. Summary results are presented in Fig. 2. This figure shows overall hydrogen production efficiencies, based on high heating value, plotted as a function of reactor outlet temperature. The figure includes a curve that represents 65% of the thermodynamic maximum efficiency [5], assuming $T_L = 20^\circ\text{C}$ (T_{low}). Three different advanced-reactor/power-conversion combinations were considered: a helium-cooled reactor coupled to a direct recuperative Brayton cycle, a supercritical CO_2 -cooled reactor coupled to a direct recompression cycle, and a sodium-cooled fast reactor coupled

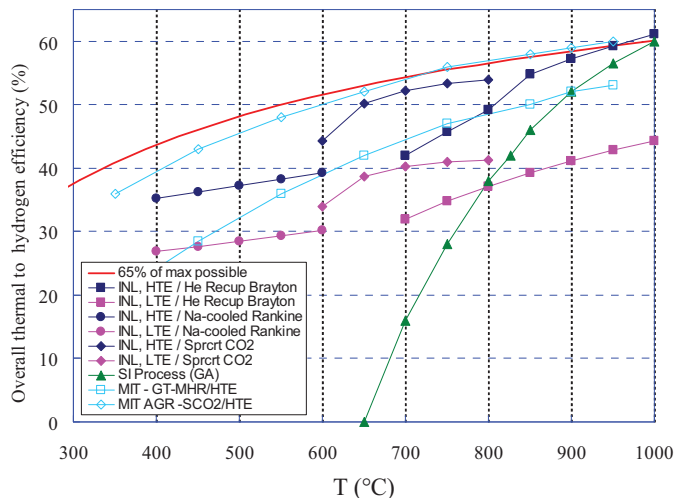


Figure 2. Overall thermal-to-hydrogen production efficiencies based on HHV for several reactor/process concepts, as a function of reactor outlet temperature.

to a Rankine cycle. The reactor outlet temperature for a conventional pressurized water reactor would be at the low end of the range shown in Fig. 2. The system analyses were performed using UniSim [15] software. Each reactor/power-conversion combination was analyzed over a reactor outlet temperature range appropriate for the power conversion system under consideration. The figure shows results for both HTE and low-temperature electrolysis (LTE). Results of system analyses performed at MIT [16] are also shown. The lower MIT curve, labeled MIT-GT-MHR/HTE represents overall efficiency predictions for a helium-cooled reactor with a direct Brayton cycle power conversion unit. The upper MIT curve, labeled MIT-AGR-SCO₂/HTE represents overall efficiency predictions for a CO₂-cooled advanced gas reactor with a supercritical CO₂ power conversion unit.

decreasing temperature, and falls below values for LTE coupled to high-temperature reactors for outlet temperatures below 800°C. Note that even LTE benefits from higher reactor outlet temperatures because of the improved power conversion thermal efficiencies associated with higher reactor outlet temperatures. Current planning for the Next Generation Nuclear Plant (NGNP) [18] indicates that reactor outlet temperatures will be at or below 800°C, which favors HTE.

Bio-Syntrolysis. The second concept presented in this paper is based on biomass gasification rather than pyrolysis. It is a unique hybrid energy concept, termed Bio-Syntrolysis, which enables efficient carbon-neutral production of synthetic liquid fuels from non-food biomass and electrical energy. A schematic process diagram for Bio-Syntrolysis is shown in Fig. 3. The process fully converts cellulosic recyclable non-

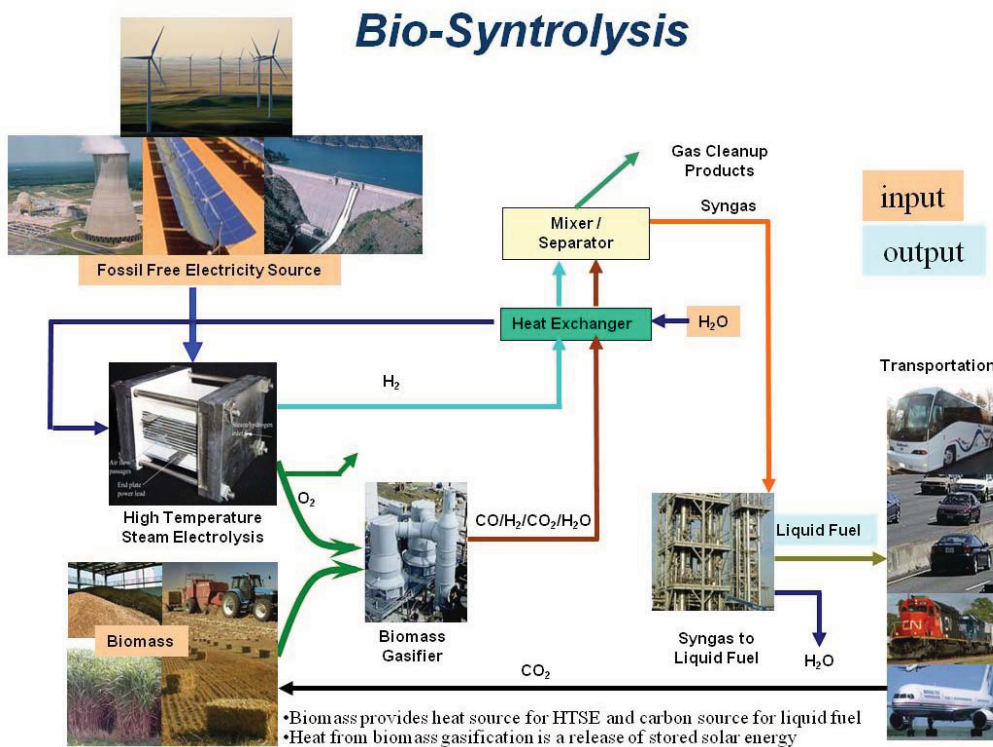


Figure 3. Bio-Syntrolysis Process Diagram.

For reactor outlet temperatures of 600 - 800°C, the supercritical CO₂/recompression power cycle is superior to the He-cooled/Brayton cycle concept. This conclusion is consistent with results presented in reference [16]. Finally, an efficiency curve for the SI thermochemical process [18] is also shown. The results presented in Fig. 2 indicate that, even when detailed process models are considered, with realistic component efficiencies, heat exchanger performance, and operating conditions, overall hydrogen production efficiencies in excess of 50% can be achieved for HTE with reactor outlet temperatures above 850°C. The efficiency curve for the SI process also includes values above 50% for reactor outlet temperatures above 900°C, but it drops off quickly with

food biomass; such as barley and wheat straw, corn stover, wood chips, or energy crops; into liquid synthetic fuels for the transportation sector. A unique aspect of this process is the integration of biomass gasification with hydrogen production based on HTSE. The Idaho National Laboratory (INL) has been a world leader in developing HTSE technology for several years and has demonstrated HTSE at the bench and integrated laboratory (15 kW) scales [19]. In this concept, the high temperature process heat for HTE is provided in a synergistic fashion by the biomass gasifier while the oxygen required for the gasifier is produced as a by-product of the HTE process. Large-scale deployment of this technology would enhance energy security by reducing demand for imported oil. To the

extent that it could be powered by nuclear or renewable energy, the synthetic liquid fuel product would be carbon-neutral. The concept could operate economically using off-peak or excess power capacity, while contributing to grid stability and serving as a primary energy storage technology. Referring to Fig. 3, biomass is fed to an oxygen-blown gasifier using oxygen produced from the HTSE unit. The gasifier operation is optimized to produce as much CO as possible and to avoid producing CO₂. This process is highly exothermic such that the products exiting the gasifier provide the high-temperature process heat required for operation of the HTSE unit via a heat exchanger. The HTSE unit also requires an external input of electrical power which would be provided (ideally) using a non-fossil carbon-free source such as hydro, wind, solar, or nuclear. The syngas exiting the heat exchanger is cleaned and sent to an advanced Fischer-Tropsch (FT) reactor that produces synthetic liquid transportation fuels. The overall process achieves a carbon conversion efficiency greater than 90%, compared to 35% for traditional biomass gasification or cellulosic ethanol production. This large increase in carbon utilization is due to the addition of supplemental hydrogen to the process. Since HTSE is not immediately commercially

available, conventional low temperature electrolysis (LTE) could be used for hydrogen production in the short term with an efficiency penalty. The ultimate goal is development and deployment of a process that couples (HTSE) with Fluidized-Bed Biomass Gasification (FBBG) and advanced Fischer-Tropsch (FT) reactor technology to produce non-food biomass-based liquid fuels incorporating a substantial nuclear or renewable energy component. The process provides a means of storing non-dispatchable electrical energy as synthetic liquid bio-fuels, displacing both the CO₂ emissions (carbon neutral) and the economic drain of conventional (imported) transportation fossil fuels.

SYSTEM MODELING AND RESULTS

A process model was developed using the Honeywell UniSim process modeling software. This commercial software is used in the oil and gas industry and can model thermo-chemical systems ensuring chemical, energy and mass balances [15]. Four types of recyclable biomass were considered parametrically for this study. They are barley straw, wood bark, corn stover and switchgrass. The ultimate analysis of the dry, ash free,

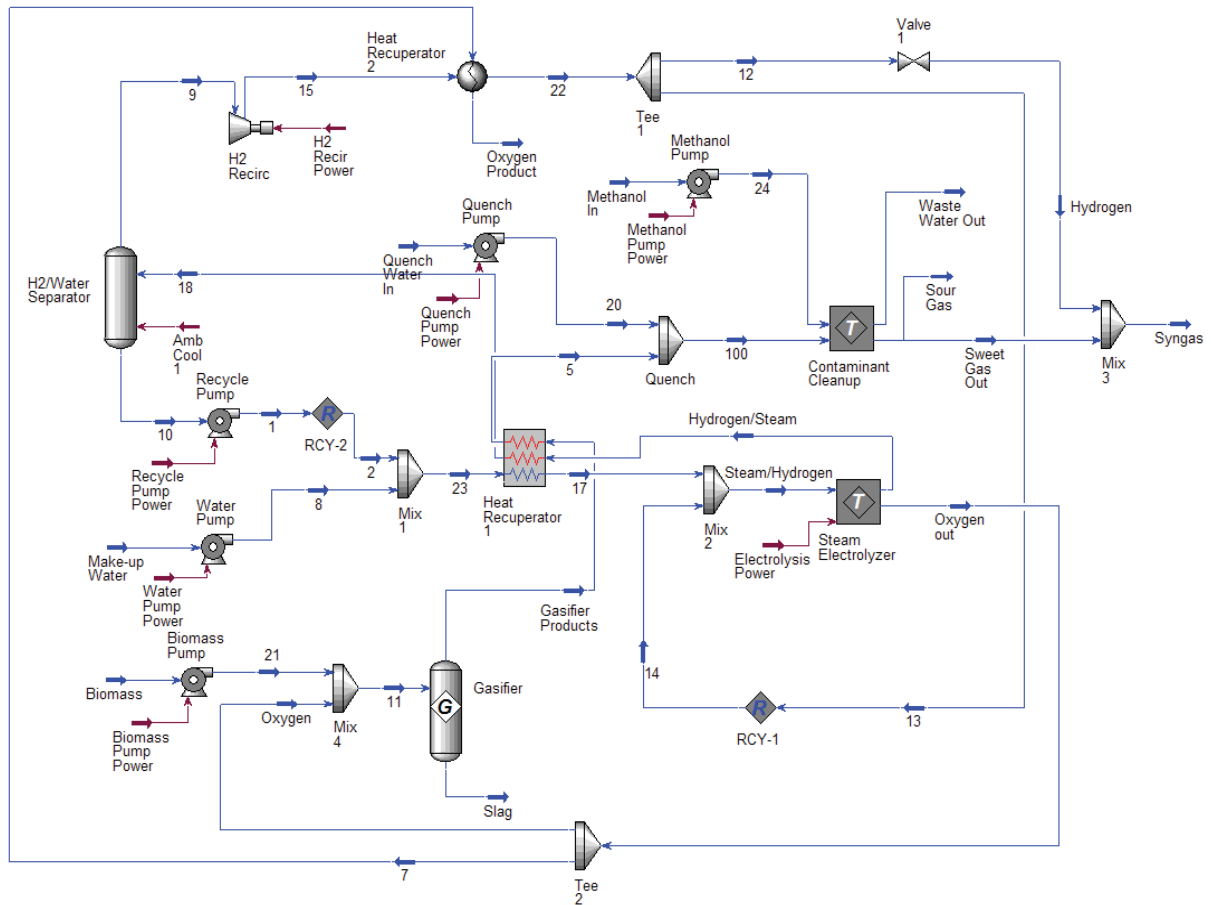


Figure 4. Process flow diagram for biomass gasification with high temperature electrolysis.

Table 1. Ultimate analysis of various recyclable biomasses.

Biomass	C (%)	H (%)	O (%)	N (%)	S (%)	Cl (%)	Ash (%)	Water (%)	LHV (kJ/kg)
Barley Straw	49.2	6.0	44.1	0.4	0.06	0.43	4.9	11.5	18460
Bark	52.1	5.8	41.4	0.57	0.03	0.016	3.3	11.5	16029
Corn Stover	49.3	6.0	43.6	0.7	0.11	0.28	5.1	11.5	17746
Switchgrass	53.2	6.4	39.0	1.3	0.11	0.0	10.1	11.5	18653

biomasses is shown in Table 1 and is based on the PHYLLIS database of the Energy Research Centre of the Netherlands [20]. Inputs from the biomass include the lower heating value. For example, the lower heating value of the barely straw is 18,460 kJ/kg. The dry ash is primarily silicon oxide with some potassium and calcium oxide. Both the ash and the dry, ash free, biomasses were modeled as hypothetical components. The composition and heating value of the biomasses are the only necessary components for the gasification process model. The gasifier uses a Gibbs reactor which minimizes the Gibbs free energy to determine the most likely products based on the composition, flow rates, pressure and temperatures of the barley straw, water, and oxygen. A large number of components were considered as products, but only those listed in Table 2 were present.

Table 2. Molar composition exiting gasifier with barley straw as biomass.

Component	% Mole Fraction
Carbon Monoxide	51.81%
Hydrogen	43.86%
Water	2.22%
Carbon Dioxide	0.99%
Nitrogen	0.20%
Hydrogen Chloride	0.16%
Methane	0.73%
Hydrogen Sulfide	242 ppm
Ammonia	24 ppm
Carbonoxysulfide	1 ppm

The primary purpose of modeling the ash is to simulate the heat captured by the ash during gasification, but the ash does not react chemically in the gasifier. A temperature dependent specific heat is determined based on the composition of the ash.

Figure 4 is the process flow diagram for biomass syngas production using high temperature electrolysis HTE. The process is scaled to a biomass feed rate of 1 kg/s. The biomass is reacted with oxygen from the steam electrolyzer at a variety of gasifier temperatures ranging from 1500 K to 1900 K. The gasification temperatures were selected to ensure chemical equilibrium and are based on temperatures for a Shell gasifier

for coal [21]. Slagging of the ash will occur at those temperatures. Just enough oxygen is added to make the gasification process adiabatic.

The gasifier product stream and the hydrogen stream from the electrolyzer exit are cooled in the Heat Recuperator 1 heat exchanger to generate steam at 1073 K for the electrolysis unit. The water entering Heat Recuperator 1 is supplied by a make-up water source that is pumped to pressure and the water recycled from the electrolyzer outlet.

Oxygen from the electrolyzer is sent to the gasifier in a controlled manner. Extra oxygen not needed goes through a cool down process. The gasifier product stream is quenched with water to the point of saturation for the purpose of modeling the energy loss due to particulate removal using a quenching process. The water contains some undesirable components from the gasifier including hydrogen sulfide and hydrogen chloride and therefore cannot be recycled. The contaminants in this stream are removed in a contaminant removal process that is based on the Rectisol process. Methanol is refrigerated to 233 K and enters the top of an absorber. The gasifier product stream is cooled to remove excess water and enters the bottom of the absorber. The refrigerated methanol captures the hydrogen sulfide, some of the carbon dioxide, the ammonia, and the hydrogen chloride. The methanol is regenerated in a distillation column which is then recycled back to the absorber. Any losses of methanol are replaced. The contaminants exit the distillation column at the top of the column as a sour gas. The heat for the reboiler of the distillation column is provided by combusting a small stream of biomass at a feed rate of 0.025 kg/s (see Figure 4). The energy used to pump and to refrigerate the methanol and the biomass burned to supply heat for the reboiler are taken into account in efficiency and carbon utilization analyses.

Hydrogen from the electrolysis process is mixed with the gasifier stream to produce a syngas of hydrogen to carbon monoxide ratio of 2. This ratio is ideal for many synthetic fuel processes such as the Fischer Tropsch, FT.

The inlet mole composition of the stream at the electrolyzer is 10% hydrogen and 90% steam. The heat from the gasifier and electricity provide the energy to split the steam into oxygen and hydrogen. The process out stream is composed of 90% hydrogen and 10% steam. The stream is cooled to near ambient temperatures by the Heat Recuperator 1. The water is separated from the hydrogen at the H₂/Water Separator. The water is recycled and mixed with the makeup

water.

The hydrogen exiting the separator is used primarily for syngas production but some is recycled to the inlet of the electrolysis process to provide reducing conditions at the water side electrode.

Pressure losses in the heat exchangers and the gasifier are set at 20 kPa per pass. An average pressure of 2.78 MPa was assumed for the analysis. The isentropic efficiencies of the pumps and hydrogen circulating compressor are set at 75%. The refrigeration compressor has an efficiency of 90%.

The steam electrolyzer is a module developed at the Idaho National Laboratory to simulate the temperature and compositional averaged Nernst potential of an electrolysis process. Details of the module are found in references [22, 23]. Given the number of cells, the area specific resistance (ASR), the current density, the cell area, and the inlet flow conditions of the process stream, the module will calculate the average Nernst potential, the per-cell operating voltage, the electrolysis power, the process heat needed and the outlet flow conditions of the hydrogen and oxygen streams. For this parametric study, it was assumed that the ASR was 0.4 ohms*cm², the current density was adjusted to provide thermal neutral conditions (adiabatic and isothermal), and the per-cell area was 225 cm². The thermal neutral conditions set the per-cell operating voltage at 1.288 Volts/cell. The number of cells was adjusted until the hydrogen to carbon monoxide syngas ratio was 2.0. Within the module, a setting was made so that 88.9% of the steam entering the electrolyzer was converted to oxygen and hydrogen resulting in an outlet stream molar composition of 90% hydrogen and 10% steam.

Supplemental hydrogen from electrolysis enables achievement of high carbon utilization such that about 95% of the carbon in the biomass feedstock is retained in the syngas product, as shown in Fig. 5 [24]. Oxygen produced from the electrolysis process is used to control the oxidation rate in the oxygen-blown biomass gasifier. Syngas production efficiencies range from 70% to 73%, depending on the gasifier temperature. Based on this technology, 1 GW of electrical power could be used to produce 25,000 barrels/day of synthetic liquid fuel.

Biomass is bulky; hauling distances must be kept small. Therefore, utilization of biomass as a renewable energy source for synthetic fuels production will require distributed regional processing. A regional bio-syntrolysis concept is shown in Fig. 6. This concept shows a centrally located nuclear reactor serving as the primary energy source for carbon-free electric power (and process heat) generation. In the regional concept, SMRs could be sized and distributed based on economic optimization.

KEY TECHNICAL AREAS FOR DEVELOPMENT

Process Design & Simulation. Preliminary flow sheet analysis and simulation of the Bio-Syntrolysis process has been performed at the INL [24]. The process design elements need to be integrated and optimized from the perspective of process efficiency and overall system economics. There are a large number of possible cross connections of the mass and energy flows between the three main process elements: gasifier, electrolyzer and FT synthesis unit.

Design and simulation analysis objectives:

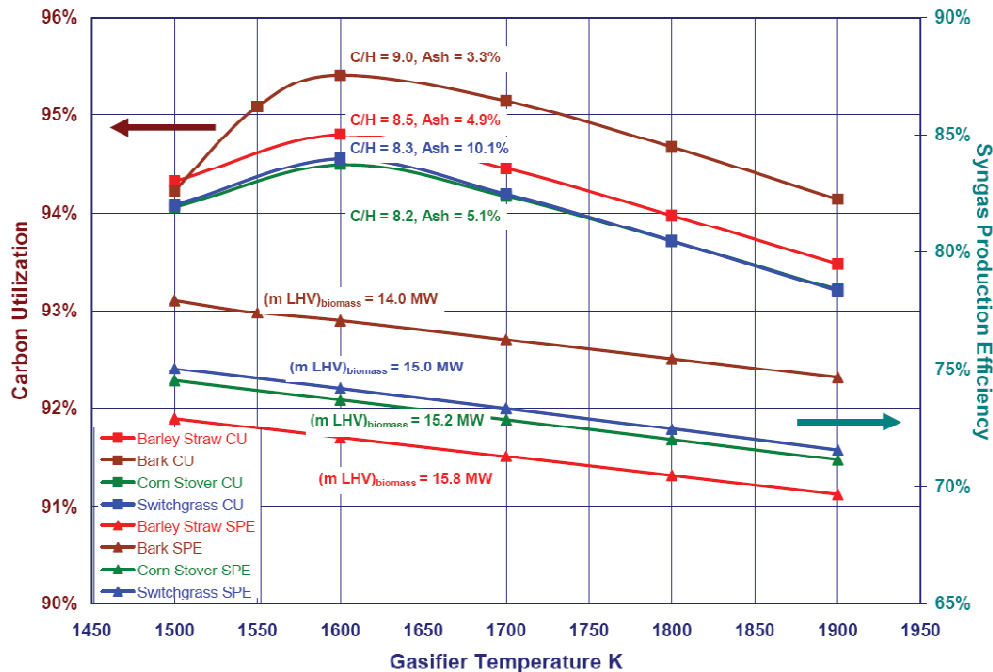


Figure 5. Carbon utilization and syngas production efficiency for various biomass feedstocks as a function of gasifier temperature (from [24]).



Figure 6. Bio-Syntrolysis Regional Concept

1. Identification of potentially advantageous integrated process configurations.
2. Relative sizing and specification of the process duty of the gasifier, electrolysis, and FT units.
3. Determination of the relative demand for biomass feedstock, water, electric power, and process heat on a product basis.
4. Quantitative estimates of energy storage efficiency.
5. Preliminary economic feasibility estimates.
6. Unit operations model validation using available experimental data.

Electrolysis Unit Development. The INL has been the lead laboratory for research, development and demonstration of HTSE technology under the DOE Nuclear Hydrogen Initiative and NNGP. However, much of this work has been driven by the vision of large central hydrogen production plants directly coupled to an advanced high temperature reactors and power conversion units for electricity and high temperature process heat. Since the required process heat for bio-syntrolysis is supplied by the gasifier, the concept does not require any external high temperature process heat. The only required external energy addition is electric power. Regardless of the specific application, the research and development challenges for HTSE are the same: increase stack performance and lifetime, minimize system cost.

In addition, there are some unique challenges associated with the proposed HTSE application. Operation of the stack without a sweep gas on the oxygen evolution stream will be necessary in order to deliver a pure oxygen byproduct to feed the gasifier. Such a change will impact process heat exchange design, materials selection of process piping for compatibility with a high temperature pure oxygen, and to a lesser extent the electrochemical and materials response within the stack. Stack testing in this mode of operation has not been routinely

demonstrated, so a hazards analysis and expanded testing are needed. An alternative would be to use steam as a sweep gas and condense it out upstream of the gasifier.

Gasification Unit Development. The INL has performed considerable research and experimentation on feedstock preparation for delivery to biomass gasifiers. The effects of moisture content, particle size, bulk density, and feedstock type have been examined. Evenly flowable biomass and the equipment to handle that biomass have been successfully demonstrated. Various oxygen-blown biomass gasifiers are commercially available. Modeling and optimization will be key in selecting the appropriate gasifier for the Bio-Syntrolysis process.

Fischer-Tropsch Unit Design and Development. The economic biomass collection radius will determine the optimum size of a Bio-Syntrolysis plant. A significant aspect of a FT reactor design is the approach taken to remove heat from the highly exothermic FT reactions. This in turn will vary depending on the reactor size and process heat integration considerations. A FT reactor cooling and catalyst loading configuration will be developed to match the anticipated plant scale and process integration options being considered. The FT reactor will be sized to process the combined syngas production from the gasifier and electrolysis units. Experimental work on a representative repeat element of the FT reactor will be used to project reactor throughput, lifetime and product distributions under the anticipated operating conditions (temperature, pressure, syngas bulk composition and impurities).

The reactor will also serve as a test bed for catalyst preparation process development. As a member of the BYU Fischer-Tropsch Consortium, the INL has access to a wealth of FT catalyst preparation and characterization data. The INL has experience in producing and characterizing FT catalysts.

However, consistent with the systems-level aims of this project, this effort will focus on using historically proven FT catalyst formulations rather than searching for a novel breakthrough catalyst.

SUMMARY AND CONCLUSIONS

Two concepts for cellulosic biomass-based synthetic liquid fuels production have been presented. These hybrid energy system concepts enable storage of nuclear energy from small modular reactors in the form of transportation fuels, enhancing energy security while reducing greenhouse gas emissions. Exploitation of biomass resources for synthetic fuels production requires a distributed concept. The first of the two concepts uses nuclear process heat for biomass hydropyrolysis and supporting processes including high temperature electrolysis for supplemental hydrogen production. The second process uses electricity from the nuclear power plant and a power conversion unit to operate an HTSE process that is thermally integrated with a biomass gasification unit. In this concept, the HTSE unit supplies the carbon-free supplemental hydrogen required to achieve high process efficiency and high carbon utilization. It also supplies oxygen for an oxygen-blown biomass gasifier. The gasifier in turn synergistically provides the high-temperature process heat needed to maintain the high operating temperature of the HTSE unit. Hydrogen from the HTSE unit is added to CO from the gasifier making a syngas mixture ready for liquid fuel production via the Fischer-Tropsch process. Results of preliminary system analysis indicate that high carbon utilization and high efficiency can be achieved.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Nuclear Hydrogen Initiative and Next Generation Nuclear Plant Programs under DOE Operations Office Contract DE-AC07-05ID14517.

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REFERENCES

- [1] O'Brien, J. E., "Large Scale Hydrogen Production from Nuclear Energy using High Temperature Electrolysis," Keynote Lecture and Proceedings, 14th International Heat Transfer Conference, August 8-13, 2010, Washington DC.
- [2] Duffey, R. B., "Nuclear production of hydrogen: When worlds collide," *International Journal of Energy Research*, Vol. 33, pp. 126-134, 2009.
- [3] Granovskii, M., Dincer, I., and Rosen, M. A., "Greenhouse gas emissions reduction by use of wind and solar energies for hydrogen and electricity production: economic factors," *Int. J. Hydrogen Energy*, V. 32, 2007, pp. 927-931.
- [4] Floch, P-H., Gabriel, S., Mansilla, C., and Werkoff, F., "On the production of hydrogen via alkaline electrolysis during off-peak periods," *Int. J. Hydrogen Energy*, Vol. 32, 2007, pp. 4641-4647.
- [5] O'Brien, J. E., "Thermodynamic Considerations for Thermal Water Splitting Processes and High-Temperature Electrolysis," 2008 ASME International Congress and Exposition, paper# IMECE2008-68880, Boston, Nov., 2008.
- [6] "Multi Year Program Plan 2007-2012," Office of the Biomass Program Energy Efficiency and Renewable Energy, U.S. Department of Energy, August 31, 2005, http://www.inl.gov/bioenergy/reports/d/1012_mypp_07-12.pdf
- [7] Terry Marker, et. al., "Direct Production of Gasoline and Diesel from Biomass using Integrated Hydropyrolysis and Hydroconversion (IH2)," Gas Technology Institute, Des Plaines, Illinois, United States, U.S. DOE Award DE-EE-0002873.
- [8] Herring, J. S., O'Brien, J. E., Stoots, C. M., and Hawkes, G. L., "Progress in High-Temperature Electrolysis for Hydrogen Production using Planar SOFC Technology," 2005 AIChE Spring Annual Meeting, April 10 – 14, 2005, Atlanta, GA.
- [9] Varrin, R. D., Reifsneider, K., Scott, D. S., Irving, P., and Rolfson, G., "NGNP Hydrogen Technology Down-Selection; Results of the Independent Review Team Evaluation," Dominion Engineering report# R-6917-00-01, August, 2009.
- [10] Stoots, C. M., O'Brien, J. E., "Results of Recent High-Temperature Co-electrolysis Studies at the Idaho National Laboratory," *International Journal of Hydrogen Energy*, Vol. 34, Issue 9, pp. 4208-4215, May 2009.
- [11] Steinfeld, A. "Solar thermochemical production of hydrogen," *Solar Energy*, V 78, No 5, pp. 603-615, May 2005.
- [12] Hawkes, G. L. and McKellar, M. G., "Liquid Fuel Production from Biomass via High Temperature Steam Electrolysis," 2009 AIChE Annual Meeting, November 8 – 13, 2009, Nashville, TN.
- [13] O'Brien, J. E., "Review of the Potential of Nuclear Hydrogen for Addressing Energy Security and Climate Change," *Nuclear Technology*, in review, 2010.

- [14] Stoots, C. M., O'Brien, J. E., Condie, K. G., and Hartvigsen, J. J., "High-Temperature Electrolysis for Large-Scale Hydrogen Production from Nuclear Energy – Experimental Investigations," *International Journal of Hydrogen Energy*, Vol. 35, Issue 10, pp. 4861-4870, May 2010.
- [15] UniSim Design, R360 Build 5, Honeywell International Inc., Copyright 2005-2006.
- [16] Yildiz, B., and Kazimi, M. S., "Efficiency of Hydrogen Production Systems Using Alternative Nuclear Energy Technologies," *Int. J. of Hydrogen Energy*, Vol. 31, pp. 77-92, 2006.
- [17] Brown, L. C., Lentsch, R. D., Besenbruch, G. E., Schultz, K. R., "Alternative Flowsheets for the Sulfur-Iodine Thermochemical Hydrogen Cycle," *AIChE Journal*, April 2003.
- [18] Southworth, F., Macdonald, P. E., Harrell, D. J., Park, C. V., Shaber, E. L., Holbrook, M. R., and Petti, D. A., "The Next Generation Nuclear Plant (NGNP) Project," *Proceedings, Global 2003*, pp. 276-287, 2003.
- [19] Stoots, C. M., O'Brien, J. E., Condie, K., Moore-McAteer, L., Housley, G. K., Hartvigsen, J. J., and Herring, J. S., "The High-Temperature Electrolysis Integrated Laboratory Experiment," *Nuclear Technology*, Vol. 166, No. 1, pp. 32 – 42, April, 2009.
- [20] PHYLLIS, ECN-Biomass, Version 4.13, Energy Research Centre of the Netherlands (ECN), www.ecn.nl/phyllis.
- [21] Suidevel, P. L., "Shell Coal Gasification Process for Power and Hydrogen/Chemicals." GTC Conference, Washington D.C., October 2004.
- [22] O'Brien, J. E., McKellar, M. G., Hawkes, G. L., and Stoots, C. M., "Development of a One-Dimensional Co-Electrolysis Model for Use in Large-Scale Process Modeling Analysis," *Fifth International Conference on Fuel Cell Science, Engineering & Technology*, June 18-20, 2007, New York, USA.
- [23] O'Brien, J. E., McKellar, M. G., Stoots, C. M., Herring, J. S., and Hawkes, G. L., "Parametric Study of Large-Scale Production of Syngas via High Temperature Electrolysis," *International Journal of Hydrogen Energy*, Vol. 34, pp. 4216-4226, May, 2009.
- [24] McKellar, M. G., Hawkes, G. L., and O'Brien, J. E., "The Production of Syngas via High-Temperature Electrolysis and Bio-Mass Gasification," *2008 ASME International Mechanical Engineering Congress and Exposition*, paper# IMECE2008-68900, Boston, MA, Nov., 2008.