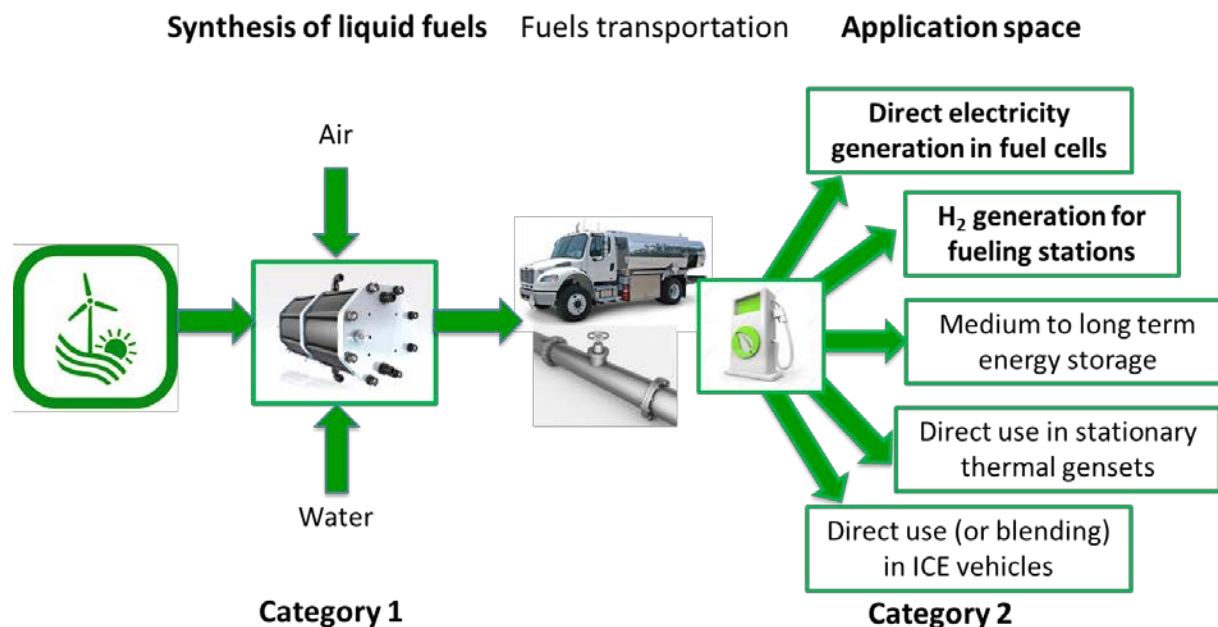


# Renewable Energy to Fuels Through Utilization of Energy-Dense Liquids (REFUEL) Program Overview

## B. PROGRAM OVERVIEW

### 1. SUMMARY

The purpose of the Renewable Energy to Fuels through Utilization of Energy-dense Liquids (**REFUEL**) program is to develop scalable technologies for conversion of electrical or thermal energy from renewable sources into chemical energy contained in energy dense Carbon-Neutral Liquid Fuels (CNLF) that can be stored, transported, and later converted into hydrogen or electricity to provide power for transportation and distributed energy generation. The overall structure of the REFUEL program is illustrated in Figure 1 below. Because CNLFs can be stored for extended periods of time and then transported to consumers using existing and inexpensive technology for liquid fuel delivery and distribution, they offer a unique opportunity to reduce both the need for energy imports and carbon emissions from the transportation sector. In meeting that need, they also have the potential to enable increased penetration of intermittent renewable energy sources. The success of this program depends on developing technologies in two categories: (1) the synthesis of CNLFs using intermittent renewable energy sources and water and air (N<sub>2</sub> and CO<sub>2</sub>) as the only chemical input streams and (2) the conversion of CNLFs delivered to the end point to another form of energy (e.g. hydrogen or electricity).



**Figure 1. The production, transport and use of carbon-neutral liquid fuels for energy delivery. Areas of interest within Category 2 in this FOA are shown in bold.**

The program's overall goal is a competitive total cost (including production, transportation, storage, and conversion costs) of **delivered (source-to-use) energy** (e.g. converted to motive power for transportation) as opposed to the **primary** energy stored in chemical form **below \$0.3/kWh**, the price needed to be competitive with other carbon-free delivery methods, as will be discussed in Section B. The source-to-use energy cost (SUE) is defined here as the sum of the fuel production cost (CF), the cost of transportation or transmission from production to the user (CT), the cost of any storage (CS), divided by the conversion efficiency ( $\eta$ ) to account for any losses during the conversion steps, and the capital cost of fuel conversion (CC)<sup>1</sup>:

<sup>1</sup> In preparation for Full Application submission, please see Section I.E of the FOA for further details on the SUE analysis.

$$SUE = \frac{CF+CT+CS}{\eta} + CC \quad (1)$$

Representative values for several commercial approaches to providing transportation energy are given in Table 1 using gasoline burned in internal combustion engines (ICEs) as a baseline. The standard commercial process for producing H<sub>2</sub> (either as the final product, or as a feedstock for ammonia production) is thermochemical steam-methane reforming (SMR). The corresponding values in the table are calculated based on literature cited in the footnotes. The column titled “Electricity” is representative of moving electricity across the current grid and storing it in an electric vehicle (EV) battery. The values contained in Table 1 will be discussed further in the context of carbon-free fuels in the following sections of this document.

**Table 1:** Comparative costs of current different energy delivery options for transportation.

	Gasoline	Hydrogen by SMR	Ammonia by SMR/Haber-Bosch	Electricity
Specific energy density, kWh/kg	12.7	33.3	5.16	
Energy density, kWh/L	8.76	0.8	4.25	
Fuel cost, \$/kg	0.54 <sup>a</sup>	1.95 <sup>b</sup>	0.325 <sup>c</sup>	
Fuel cost, \$/kWh	0.047	0.058	0.063	0.065 <sup>d</sup>
Transmission cost, \$/kWh <sup>e</sup>	0.001	0.060	0.004	0.038 <sup>d</sup>
Storage cost, \$/kWh <sup>e</sup>	0.001	0.030	0.007	0.160 <sup>f</sup>
Conversion efficiency, % <sup>f</sup>	30	55	55	92
Source-to-use energy cost, \$/kWh <sup>g</sup>	0.159	0.292	0.135	0.285

<sup>a</sup> – Average production cost for 2015 in California, <http://energyalmanac.ca.gov/gasoline/margins>;

<sup>b</sup> – \$1.95/kg production cost based on SMR path: 3.1 Hydrogen Production in “DOE Multi-Year Research, Development, and Demonstration Plan” (2015) [http://energy.gov/sites/prod/files/2015/06/f23/fcto\\_myrrdd\\_production.pdf](http://energy.gov/sites/prod/files/2015/06/f23/fcto_myrrdd_production.pdf);

<sup>c</sup> – Maung, T., et al., “Economics of Using Flared vs. Conventional Natural Gas to Produce Nitrogen Fertilizer: A Feasibility Analysis”, North Dakota State University (2012) <http://ageconsearch.umn.edu/bitstream/133410/2/Department-APUC%20Report.pdf>;

<sup>d</sup> – EIA Annual Energy Outlook 2015, Table titled ‘Electricity Supply, Disposition, Prices, and Emissions for average 2015 electricity generation and T&D costs’; <http://www.eia.gov/forecasts/aeo/data/browser/#/?id=8-AEO2015>

<sup>e</sup> – transportation and storage costs calculated using data from: Curley, M., Pipeline and Gas Journal (2008) 235, 34; Ramsden, T., et al., “Hydrogen Pathways”, NREL report TP-6A10-60528; Bartels, J. R. and Pate, M. B., “A feasibility study of implementing an Ammonia Economy”, Iowa State University, 2008; Schoenung, S., “Economic Analysis of Large-Scale Hydrogen Storage for Renewable Utility Applications”, Sandia report SAND2011-4845 (2011);

<sup>f</sup> – Nykvist, B. and Nilsson, M., Nature Climate Change, (2015), 5, 329, assumed battery pack cost of \$300/kWh, operating at one cycle per day for 8 years with a 85% round-trip efficiency (92% discharge efficiency) at 70% depth of discharge.

<sup>g</sup> – Conversion capital cost not included.

Technologies developed under the REFUEL program will enable long-term (i.e. multi-day capacity) energy storage and long-distance renewable energy delivery from remote, isolated, and/or stranded locations and create an affordable refueling infrastructure of clean fuels. Furthermore, all of these applications will support the goal of substantially reducing carbon emissions. Implementation of the aggressive targets of the REFUEL program will require R&D teams to be built from several communities, including: electrocatalysis, heterogeneous catalysis, materials science, electrochemical systems design, gas separation, process engineering, and systems integration.

## 2. PROGRAM MOTIVATION

Chemicals, such as hydrocarbons, are effective energy carriers and return the largest fraction of their energy density when delivered via a pipeline. However, fossil fuels are major CO<sub>2</sub> emitters and also drive energy imports. Reducing energy imports from foreign sources and energy-related emissions, including greenhouse gas (GHG) emissions, which are part of ARPA-E’s mission, could be achieved by: (1) shifting to cleaner transportation fuels, e.g. hydrogen and biofuels; (2) increased use of low-carbon electricity generation forms, e.g. solar and wind; and (3) enhancements in the efficiency and reliability of U.S. electric power distribution system. REFUEL targets areas (1) and (2) with ancillary benefits for area (3).

We define CNLFs in this FOA as: hydrogen-rich liquid fuels made by converting molecules contained in air (N<sub>2</sub>, CO<sub>2</sub>) and hydrogen from water into energy-carrying liquids at moderate temperatures and pressures using renewable energy sources. Hydrogen is the simplest chemical that can be considered for use as a CNLF (in liquid form), and stationary fuel cells and vehicles using hydrogen as a fuel are maturing technologies.<sup>2</sup> The standard commercial process for producing H<sub>2</sub> is thermochemical steam-reforming of methane (SMR). H<sub>2</sub> produced in this way is not a carbon neutral fuel, as the chemical process produces one molecule of CO<sub>2</sub> for every four H<sub>2</sub> molecules,<sup>3</sup> and the thermal energy necessary for the process is provided by CO<sub>2</sub> emitting fossil fuel sources. Generation of carbon-neutral hydrogen is possible using electrolysis of water, if the electricity is provided from renewable sources such as wind or solar, or from nuclear energy.<sup>4</sup> Currently, the most advanced method for H<sub>2</sub> production is either polymer electrolyte membrane (PEM) or alkaline water electrolysis.

Clean hydrogen is used in commercial fuel cell electric vehicles (FCEV) to achieve carbon-neutral transportation.<sup>5,6</sup> However, the limitations of hydrogen storage and transportation, which will be described below, have limited the growth of a hydrogen infrastructure, generating a hurdle to widespread adoption of FCEVs.<sup>7,8</sup> This infrastructure will not be built while the number of FCEVs using it remains low (classic “chicken and egg” problem).

Because of the inherent difficulties in achieving zero-carbon emissions with fossil fuels in the transportation sector, we must consider new options. The REFUEL program seeks to address these challenges by developing CNLFs that provide a new set of technology options for storing renewable energy in CNLFs, and delivering it economically and effectively when and where it is needed.

The following section provides examples technologies and their impact with respect to four topic areas: (1) hydrogen for energy storage and deliver; (2) opportunities for CNLFs; (3) delivery of energy services from CNLFs; and (4) ancillary benefits in integration of renewable power sources.

### Hydrogen for energy storage and delivery

Chemical energy storage in hydrogen can be combined with energy transmission in the form of a compressed gas or a cryogenic liquid. Some relevant properties of hydrogen are listed in Table 2, with a comparison to gasoline, ethanol, and a potential alternative CNLF (described below). Hydrogen has extremely high specific energy (39.4 kWh/kg, HHV) but a rather low volumetric energy density (theoretical values are 2.28 kWh/L as a liquid and 1.55kWh/L as gas at 700 bar, which is reduced to 1.7 and 0.8 kWh/L in practical systems).<sup>9</sup> The only industrial carbon-neutral method of hydrogen production is water electrolysis, when electricity is generated by renewable sources, using commercial PEM or alkaline electrolyzers or emerging solid oxide electrolytic cells (SOEC). Hydrogen can be utilized in a variety of fuel cells, e.g. PEM fuel cells or solid oxide fuel cells (SOFC) and, with lower efficiency, in internal combustion engines or turbines for both stationary and mobile applications. One disadvantage of hydrogen is the 30 – 45% round trip efficiency (RTE) due to the less than 70% generation efficiency water electrolysis to form hydrogen and the 55 – 65% conversion efficiency in fuel cells to produce electricity.

<sup>2</sup> Fayaz, H. et al., “An overview of hydrogen as a vehicle fuel”, *Renewable and Sustainable Energy Reviews* (2012) 16, 5511; Cipriani, G. et al., “Perspective on hydrogen energy carrier and its automotive applications”, *Int. J. Hydrogen Energy* (2014) 39, 8482.

<sup>3</sup> “Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming”, NREL Report TP-570-27637, (2001).

<sup>4</sup> Hydrogen generation from biomass (reforming of bio-derived liquids, photolytic and photosynthetic biological production, and microbial-aided electrolysis) has a potential to be zero- or low-carbon but these technologies are far from commercial readiness. Tanksale, A. et al., “A review of catalytic hydrogen production processes from biomass”, *Renewable and Sustainable Energy Reviews* (2010) 14, 166.

<sup>5</sup> National Research Council. *Transitions to Alternative Vehicles and Fuels*. Washington, DC: National Academies Press, (2013).

<sup>6</sup> [http://www.nap.edu/catalog.php?record\\_id=18264](http://www.nap.edu/catalog.php?record_id=18264)

<sup>7</sup> “Technology assessment: medium- and heavy-duty fuel cell electric vehicles”, California Air Resource Board (2015).

<sup>8</sup> Only 14 public hydrogen refueling stations exist across the U.S. today, <http://www.afdc.energy.gov>

<sup>8</sup> California proposes to build 100 additional stations by 2025 [http://www.energy.ca.gov/releases/2014-05-01\\_hydrogen\\_refueling\\_stations\\_funding\\_awards\\_nr.html](http://www.energy.ca.gov/releases/2014-05-01_hydrogen_refueling_stations_funding_awards_nr.html)

<sup>9</sup> Satyapal, S., et al., *Catalysis Today* (2007), 120, 246

**Table 2:** Properties of current and potential transportation fuels.

	Gasoline <sup>a</sup>	Ethanol <sup>b</sup>	H <sub>2</sub> (SMR) <sup>c</sup>	H <sub>2</sub> (electrolysis) <sup>c</sup>	NH <sub>3</sub> (SMR/Haber-Bosch) <sup>d</sup>	NH <sub>3</sub> (electrolysis/ Haber-Bosch) <sup>e</sup>
Process energy, MWh/ton	1.5	2.39	50.7	55	7.8	9.5
Fuel synthesis EE, % <sup>f</sup>	88	70 <sup>g</sup>	79 <sup>h</sup>	70	66	54
CO <sub>2</sub> emissions, g/kWh	338 <sup>i</sup>	104 – 273 <sup>i</sup>	357 <sup>h</sup>	0 – 114 <sup>j</sup>	310	0 – 178 <sup>j</sup>
Storage pressure, bar	1	1	700	700	10	10
Compression losses, % <sup>k</sup>	0	0	7 – 19	7 – 19	2 – 3	2 – 3

<sup>a</sup> – General Motors Corporation, Argonne National Laboratory, BP, ExxonMobil, and Shell, “Well-to-Wheel Energy Use and Greenhouse Gas Emissions of Advanced Fuel/Vehicle Systems: A North American Analysis, Volume 3, Well-to-Tank Energy Use and Greenhouse Gas Emissions of Transportation Fuels,” ANL/ES/RP-104528 (2001).

<sup>b</sup> – DOE Alternative Fuels Data Center, [http://www.afdc.energy.gov/fuels/ethanol\\_fuel\\_basics.html](http://www.afdc.energy.gov/fuels/ethanol_fuel_basics.html)

<sup>c</sup> – Ramsden, T. et al., “Hydrogen Pathways”, NREL report TP-6A10-60528

<sup>d</sup> – Bartels, J.R. and Pate, M.B., “A feasibility study of implementing an Ammonia Economy”, Iowa State University, 2008;

<sup>e</sup> – Morgan, E.R., “Techno-Economic Feasibility Study of Ammonia Plants Powered by Offshore Wind” (2013). Dissertations. Paper 697; [http://scholarworks.umass.edu/open\\_access\\_dissertations/697](http://scholarworks.umass.edu/open_access_dissertations/697); Matzen M, et al., *J. Adv. Chem. Eng.* (2015) 5, 128.

<sup>f</sup> – Energy efficiency (EE) is defined as  $EE = P/(P+E)$  where  $P$  is the primary energy of extracted hydrogen and  $E$  is energy consumed for the conversion process.

<sup>g</sup> – Gallagher, P.W. et al., “2015 Energy Balance for the Corn-Ethanol Industry”, USDA (2016)

<http://www.usda.gov/oce/reports/energy/2015EnergyBalanceCornEthanol.pdf>

<sup>h</sup> – Spath, P. and Mann, M., “Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming”, NETL report TP-570-27637 (2001).

<sup>i</sup> – Wang, M. et al., “Well-to-wheels energy use and greenhouse gas emissions of ethanol from corn, sugarcane and cellulosic biomass for U.S. use”, *Environ. Res. Lett.* (2012) 7, 045905.

<sup>j</sup> – The value is 0 if for all energy comes from renewable electricity. Higher values are if fossil fuels are used for heating and compression.

<sup>k</sup> – Percentage of energy contained in a fuel

Hydrogen compression and, especially, liquefaction incur additional energy losses (up to 10 and 35%, respectively). In contrast to liquid H<sub>2</sub>, which boils-off with a rate of 1 – 4% per day depending on the tank,<sup>10</sup> hydrogen storage and transportation as a compressed gas has very low losses. Therefore, the latter is a more attractive option for long-term storage (from days to seasonal). Average cost of hydrogen transportation via a 750 mile long pipeline is estimated to be \$1 – 2/kg H<sub>2</sub> or \$0.03 – 0.06/kWh,<sup>11</sup> which is substantially more expensive than pipeline transportation of gasoline (about \$0.025/gal or \$0.001/kWh)<sup>12</sup> or ammonia (\$34/ton per 1000 miles or \$0.004/kWh for 750 miles).<sup>13</sup>

### Opportunities for CNLFs

The use of energy-dense liquids, e.g. liquid ammonia or renewable hydrocarbons, with a similar RTE may be an attractive alternative to H<sub>2</sub>, due to the absence of or low compression losses. Storage and transportation costs can be even lower if the carbon-neutral production cost is higher than that of H<sub>2</sub>. Such CNLFs could be used in appropriately designed fuel cells. Alternatively, the costs of compression and storage, which is the major cost of the H<sub>2</sub> refueling station,<sup>14</sup> can be

<sup>10</sup> Zhang, J., et al., *J. Heat Transfer* (2005) 127, 1391.

<sup>11</sup> Amos, W., “Costs of Storing and Transporting Hydrogen”, NREL report TP-570-25106 (1998); Ramsden, T. et al., “Hydrogen Pathways”, NREL report TP-6A10-60528 (2013).

<sup>12</sup> Curley, M. *Pipeline and Gas Journal* (2008) 235, 34.

<sup>13</sup> J. R. Bartels, M. B. Pate, A feasibility study of implementing an Ammonia Economy (2008) Iowa State University, <https://nh3fuel.files.wordpress.com/2013/07/bartels-dec2008-implementinganammoniaeconomy.pdf>

<sup>14</sup> Hydrogen Station Compression, Storage, and Dispensing Technical Status and Costs. NREL report BK-6A10-58564 (2014).



reduced by using with CNLFs as hydrogen carriers and the existing liquid fuel infrastructure technologies. An ANL/TIAX analysis of hydrogen delivery, using liquid hydrogen carriers with a hydrogen content of 6 – 7 wt.%, showed that the carrier hydrogen delivery cost will be lower than liquid or compressed (700 bar) hydrogen.<sup>15</sup> CNLFs with higher hydrogen content will be even less costly. Some examples of potential CNLFs are presented in the following section.

The fuels discussed in this section are representative examples of the types of fuels that would be deemed responsive to this FOA, but this are not intended to be an exhaustive list.

Some promising CNLFs are already manufactured thermochemically at a large commercial scale (at least several thousand tons per year). The second most manufactured chemical in the world, ammonia (NH<sub>3</sub>), is produced at large-scale Haber-Bosch plants. Production volume is 160 million tons per year with 9.6 million tons produced in the U.S..<sup>16</sup> Hydrogen is combined with nitrogen over a catalyst at temperatures ranging from 380 to 520 °C and pressures ranging from 150 to 250 bar, Equation (2).<sup>17,18</sup> Optimization of process temperatures and pressures, as well as catalyst material developments over the years have resulted in 30% efficiency improvements, but the process still accounts for 1 – 2% of global energy consumption.<sup>19</sup>



Modern Haber-Bosch plants, using hydrogen generation by SMR, release about 1.6 – 1.8 ton CO<sub>2</sub> per ton of NH<sub>3</sub> of which only 0.95 ton comes from the SMR process and the rest from heating and pressurization needs.<sup>20</sup> Energy consumption for NH<sub>3</sub> production using SMR varies from 7.8 to 10.5 MWh per ton of NH<sub>3</sub> (including feedstock, which accounts for 80% of energy).<sup>21</sup> A potentially greener technology option of using hydrogen from water electrolysis requires 9.5 MWh to make 1 metric ton NH<sub>3</sub><sup>22</sup> (of which 8.9 MWh comes from hydrogen production, assuming 50.2 kWh/kg H<sub>2</sub>).<sup>23</sup> Solid-state electrochemical ammonia synthesis, a possible alternative to the Haber-Bosch process, has potentially lower energy input and operational pressure and temperature<sup>24</sup> thus simplifying the balance of plant, and could be cost competitive as long as the reaction rate is significantly increased.

Ammonia is in the liquid state below -33 °C or under 15 bar at ambient temperature and has an energy density of 4.25 kWh/L. This value is 35% higher than the energy density of liquid hydrogen (in reality the difference is even larger due to large energy requirements for H<sub>2</sub> liquefaction) and 2.5 times higher than that of hydrogen compressed to 700 bar. It is widely used as a fertilizer, a refrigerant, and a feedstock for the chemical industry. The use of ammonia as a fuel, energy carrier and hydrogen storage material has also been widely discussed.<sup>25,26,27</sup>

<sup>15</sup> Ahluwalia, R. K., et al., “Technical Assessment of Organic Liquid Carrier Hydrogen Storage Systems for Automotive Applications” ANL/TIAX report, (2011).

<sup>16</sup> <http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2011-nitro.pdf>

<sup>17</sup> Smil, V., *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*, MIT Press (2004). ISBN 9780262693134.

<sup>18</sup> Himstedt, H. H., et al., U.S. Patent Application 20150125377.

<sup>19</sup> Smil, V., *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*, MIT Press (2004). ISBN 9780262693134.

<sup>20</sup> EIA data: [http://www.iea.org/publications/freepublications/publication/tracking\\_emissions.pdf](http://www.iea.org/publications/freepublications/publication/tracking_emissions.pdf); EPA data:

<https://www3.epa.gov/climatechange/Downloads/ghgemissions/US-GHG-Inventory-2012-Chapter-4-Industrial-Processes.pdf>

<sup>21</sup> Rafiqul, I., et al, “Energy efficiency improvements in ammonia production—perspectives and uncertainties” *Energy* (2005) 30, 2487; <http://ietd.iipnetwork.org/content/ammonia#benchmark>.

<sup>22</sup> Bartels, J. R., Pate, M. B. “A feasibility study of implementing an Ammonia Economy”, Iowa State University, 2008.

<sup>23</sup> Grundt, T., and K. Christiansen. *Int. J. Hydrogen Energy* (1982) 7.3, 247.

<sup>24</sup> Giddey, S., et al, *Int. J. Hydrogen Energy* (2013) 38, 14576; Garagounis, I., et al, *Front. Energy Res.* (2014) 2, 1;

<http://dx.doi.org/10.3389/fenrg.2014.00001>; Renner, J. N., *Electrochem. Soc. Interface* (Summer 2015) 51-57

<sup>25</sup> Thomas, G. and Parks, G., U.S. Department of Energy Report (2006) [http://www.hydrogen.energy.gov/pdfs/nh3\\_paper.pdf](http://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf); Olson, N., and Holbrook, J. (2007) [http://www.powershow.com/view/5b55a-MWZjz/NH3\\_The\\_Other\\_Hydrogen\\_TM\\_powerpoint\\_ppt\\_presentation](http://www.powershow.com/view/5b55a-MWZjz/NH3_The_Other_Hydrogen_TM_powerpoint_ppt_presentation); Klerke, A., et al, *J. Mater. Chem.* (2008) 18, 2304; Bartels, J.R., Graduate Theses and Dissertations. Iowa State University, Paper 11132 (2008); Lan, R., et al, *Int. J. Hydrogen Energy* (2012) 37, 1482; Lan, R. and Tao, S. *Front. Energy Res.*, (2014) 2:35 <http://dx.doi.org/10.3389/fenrg.2014.00035>

<sup>26</sup> Ammonia is considered non-flammable by DOT classification (Class 2.2: Non-flammable compressed gas) and quickly dissipates into atmosphere if a leak does occur. It can be detected by a strong pungent smell by most people in concentrations of about 1 ppm, which is well below its harmful limits (300 ppm).<sup>See</sup> “Comparative Quantitative Risk Analysis of Motor Gasoline, LPG, and Anhydrous Ammonia as an Automotive Fuel”, Quest Consultants Inc., Norman, Oklahoma, June, 2009

<sup>27</sup> Independent studies concluded that the hazards and risks associated with the truck transport, storage, and dispensing of refrigerated anhydrous ammonia are similar to those of gasoline and LPG Duijm, .N. J., et al, “Safety assessment of ammonia as a transport fuel” (Denmark. Forskningscenter Risoe) (2005)

Another example of a nitrogen-based energy-dense fuel is hydrazine hydrate ( $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ ). It is currently produced by oxidation of ammonia at a large scale (80,000 ton/year globally) and is therefore more expensive than ammonia. However, it has a high energy density (3.56 kWh/L), is easy to handle (freezing point  $-51.7\text{ }^\circ\text{C}$ , flash point  $74\text{ }^\circ\text{C}$ ) and, if low-cost synthetic methods are developed, it may fit the technical targets of this FOA. To accomplish wide-scale implementation of CNLFs, technological advances in both the production and conversion of this fuel would need to be achieved. An example of a non-toxic substitute for hydrazine with low carbon footprint is carbohydrazide ( $\text{CH}_6\text{N}_4\text{O}$ ). Carbohydrazide has been used as a fuel in a fuel cell with an OCV 1.65V.<sup>28</sup>

In terms of carbon containing CNLFs, there are numerous examples that would fit the definition, such as hydrocarbon fuels such as synthetic gasoline or diesel fuel, alcohols, and dimethyl ether., The requirements are that the carbon is directly taken from the atmosphere or another sustainable  $\text{CO}_2$  source and that the fuel is produced in a one-pot chemical or electrochemical process. Current processes for production of synthetic fuels such as Fischer-Tropsch process are multi-step, very capital intensive and eventually not economical. Reducing the process complexity may allow increased efficiency and lower costs. A viable pathway to generate power (e.g. in fuel cells or ICEs as a drop-in fuel) or hydrogen should be demonstrated or adopted from literature. In addition, carbon containing CNLFs must have the potential to meet the source-to-use energy cost targets.

### Delivery of Energy Services from CNLFs

For the REFUEL program, the primary end use for a CNLF is either direct conversion to electricity in a fuel cell, or cracking to release hydrogen for subsequent use in a fuel cell to deliver carbon-free power for transportation.

#### *Conversion of CNLFs to electricity*

CNLFs may be converted into useful work after transportation and/or storage either directly or indirectly. In this FOA, direct conversion is defined as delivering the fuel to a fuel cell anode without any prior chemical conversion to generate electricity directly. Indirect conversion includes fuel that is reformed (cracked) such that hydrogen is stored/delivered at the endpoint of the transportation and distribution system for further use in fuel cells.

CNLFs can be converted to electricity using fuel cells, which are electrochemical devices in which the fuel is separated from an oxygen source by an electrolyte. The CNLF can be fed to the fuel cell anode; there it is either electrochemically oxidized directly, or converted to hydrogen which is then oxidized. Existing DOE programs in the Office of Energy Efficiency and Renewable Energy (EERE)<sup>29</sup> and the Office of Fossil Energy<sup>30</sup> have focused on low temperature PEM fuel cells and high temperature SOFCs for transportation and stationary power applications, respectively. Over the past ten years, these programs have advanced PEM and SOFC technologies in both performance and cost. In 2014, ARPA-E started the Reliable Electricity Based on ELectrochemical Systems (REBELS)<sup>31</sup> program, focusing on fuel cells operating in an intermediate temperature range of  $200 - 500\text{ }^\circ\text{C}$ .

One CNLF that has received significant attention for electrochemical conversion is ammonia. Alkaline fuel cells containing  $\text{Pt}$ <sup>32</sup> or  $\text{Ni}$ <sup>33</sup> anode electrocatalyst and operating from  $40$  to  $450\text{ }^\circ\text{C}$  have been powered with ammonia. In these studies, the peak power density ranged from  $2$  to  $40\text{ mW/cm}^2$ , which are modest values compared to PEM and SOFC devices. To increase the power density it is necessary to minimize ammonia crossover through the electrolyte. Another approach to ammonia fuel cells is with SOFCs operating around  $550 - 800\text{ }^\circ\text{C}$ . In this temperature range, ammonia is first decomposed, followed by electrochemical oxidation of hydrogen. The demonstrated peak power density on ammonia fuel was  $1028\text{ mW/cm}^2$  at  $800\text{ }^\circ\text{C}$ .<sup>34</sup> The decrease in power when switching from hydrogen to ammonia was approximately 10%. These impressive power densities show the promise of direct ammonia fuel cells.

<sup>28</sup> J. Qi et al, *ChemSusChem*, (2015) 8, 1147.

<sup>29</sup> <http://energy.gov/eere/office-energy-efficiency-renewable-energy>

<sup>30</sup> <http://energy.gov/fe/office-fossil-energy>

<sup>31</sup> <http://arpa-e.energy.gov/?q=arpa-e-site-page/view-programs>

<sup>32</sup> Silva, J., et al, *Applied Catalysis A: General* (2015), 490, 133 ; Yang, J., et al, *Journal of Power Sources*, (2014), 245, 277

<sup>33</sup> Ganley, J., *Journal of Power Sources*, (2008), 178, 44

<sup>34</sup> Liu, L., et al, *International Journal of Hydrogen Energy*, (2012), 37, 10857

Other liquid fuels including hydrazine have been used in direct fuel cells.<sup>35</sup> Ethanol, a product of biomass anaerobic digestion has been used in SOFCs with the performance similar to ammonia.<sup>36</sup> Liquid fuels such as toluene, n-decane, and synthetic diesel<sup>37</sup> as well as palm-derived biodiesel<sup>38</sup> have been shown to operate stably at 700 – 800 °C. However, the long-term stable performance of such systems will likely be a challenge, due in part to increases in ohmic resistance from coke formation.

### Generating H<sub>2</sub> from CNLFs

Generation of hydrogen from CNLFs can provide a viable path to affordable hydrogen refueling stations. Currently, about 75% of the refueling station capital cost is compression and storage.<sup>39</sup> Compressor cost sharply increases with the size, which is required for fast transfer of daily hydrogen delivery. In addition, large hydrogen compressors have so far demonstrated inadequate reliability. Continuous cracking of a CNLF to supply smaller size compressors for smaller high pressure tanks will allow modular capability and increase the station reliability. The use of liquid fuels to generate hydrogen on demand may allow dramatically reduced size and footprint of the storage and compressors. Storage of 300 kg compressed hydrogen occupies 450 sq. ft.<sup>40</sup> while the energy equivalent amount of liquid ammonia takes 10 times less space and can be placed underground in a standard 1000 gallon tank.

Cracking of ammonia is well known and is already a commercial process. In spite of high cracking temperature and expensive catalysts it is considered as viable option for hydrogen delivery.<sup>41</sup> Recently, it has been reported that inexpensive alkali metal amides may replace or reduce loading of platinum group metal (PGM)-based catalysts and substantially reduce the cracking temperature.<sup>42</sup> Another potential approach to H<sub>2</sub> generation from CNLFs is electrolysis. For example, ammonia oxidation to H<sub>2</sub> has a low potential (0.06V) and therefore has much lower energy requirements (1.55 kWh/kg H<sub>2</sub>) compared to water electrolysis.<sup>43</sup> Several approaches to liquid NH<sub>3</sub> electrolysis have been demonstrated<sup>44</sup> but the development of more effective electrocatalysts and cell designs is necessary.

CNLFs, especially hydrocarbons and ammonia, can potentially be used directly or as a blend in internal combustion engines or turbines. Such applications, including fuel blending or engine modifications that allows the direct use of non-traditional fuels are outside the scope of this FOA.

### Ancillary benefits in integration of renewable power sources

Penetration of renewables (solar, wind, biomass) has been limited by restricted power flow control options for the grid, grid resilience, intermittency, poor long-term predictability, and poor geographic matching of supply and demand. These problems can lead to curtailment of renewable production, and the use of less cost effective alternatives such as fast-ramping natural gas turbines (“peaker plants”). If the present grid structure continues, it is estimated that from 5.5%<sup>45</sup> to 21%<sup>46</sup> of variable generation (100 – 400 TWh) will be curtailed in 2050 at 50% renewables penetration. Further increasing the renewables penetration to 80% would require 95 – 115 GW of storage capacity.<sup>47</sup>

With a variety of grid modernization approaches, such as demand response, under way, it is likely that the amount of storage needed to integrate high renewable penetration will be reduced, but will still be very significant. The production of CNLFs from renewable power can potentially serve as an alternative form of energy storage, if the scale and production capacity can be matched to regional variabilities in electric power supply. Previously, it was shown that stationary fuel cells integrated

<sup>35</sup> Soloveichik, G.L., *Beilstein J. Nanotechnol.* (2014), 5, 1399

<sup>36</sup> Sponderberg-Petersen, L., and Larsen, H., *Energy solutions for sustainable development.* (2007) p. 347-356

<sup>37</sup> H. Kim, et al., *J. Electrochem. Soc.* 148 (2001) A693-A695.

<sup>38</sup> T. Quang-Tuyen, et al, *Int. J. Energy Res.* 37 (2013) 609-616.

<sup>39</sup> Parks, G., “Hydrogen Station Compression, Storage, and Dispensing Technical Status and Costs”, NREL report BK-6A10-58564 (2014).

<sup>40</sup> National Petroleum Council Report, Chapter 15 – Hydrogen, [www.npc.org/reports/FTF-report-080112/Chapter\\_15-Hydrogen.pdf](http://www.npc.org/reports/FTF-report-080112/Chapter_15-Hydrogen.pdf)

<sup>41</sup> Cheddie D., “Ammonia as a Hydrogen Source for Fuel Cells: A Review”, in “Hydrogen Energy - Challenges and Perspectives”, Chapter 13 (2012), DOI: 10.5772/47759.

<sup>42</sup> David, W. et al, *J. Am. Chem. Soc.*, (2014) 136, 13082; Guo, J., et al, *ACS Catal.* (2015) 5, 2708.

<sup>43</sup> Vitse, F., et al, *J. Power Sources* (2005) 142, 18–26.

<sup>44</sup> Hanada, N., et al, *Chem. Commun.*, (2010) 46, 7775; Little, D., et al, *Energy Environ. Sci.* (2015) 8, 2775.

<sup>45</sup> Lopez, A., et al, “U.S. Renewable Energy Technical Potentials: A GIS-Based Analysis”, NREL report TP-6A20-51946 (2012)

<sup>46</sup> GE Energy Consulting, J. Bebic et al., “Grid of the Future: Quantification of Benefits from Flexible Energy Resources in Scenarios With Extra-High Penetration of Renewable Energy”, Nov. 2014

<sup>47</sup> Augustine, et al. Renewable Electricity Generation and Storage Technologies. Vol 2. of Renewable Electricity Futures Study. NREL Report TP-6A20-52409-2 (2012).

with energy storage and demand control techniques can reduce grid instability.<sup>48</sup> Due to the significant costs of creating new electrical transmission capability, and losses in transmission, CNLF production plants would likely be placed near to sources of renewable power, and the fuels would be shipped to consumers at lower cost by truck, rail or pipeline. While the primary goal of this program is the production and conversion of CNLFs for transportation, future applications in long term storage for support of the electric power system can also be envisioned.<sup>49</sup>

## Summary

The technical approach of the **REFUEL** program is to develop novel cost- and energy-efficient technologies for generation of energy-dense liquid fuels from renewable energy, water, and air, and their subsequent conversion to deliverable power for transportation and distributed generation.

This approach will allow use of existing liquid fuel transportation technologies for transferring renewable energy from remote or stranded locations to the end-use customer instead of using electricity or hydrogen (schematically represented in Figure 1). Renewable energy such as electricity from solar and wind farms, will be converted to a CNLF (technologies of interest in Category 1), transported by existing methods, and converted via direct (electrochemical in a fuel cell) or indirect (via intermediate hydrogen extraction) oxidation at the point of use (technologies of interest in Category 2). Conceptually this program aims to minimize system level carbon emissions, and electrical transmission and storage losses, while remaining cost competitive.

The target CNLFs can be indefinitely stored in the liquid state under moderate pressure (up to 20 bar) or moderate cooling (down to -40 °C), can be transported using existing or easily expanded and modified infrastructure, and converted back into electricity and/or heat. The conversion products (primarily N<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>) are not captured and are released to the atmosphere. Fuels containing carbon are acceptable as long as the carbon is taken directly from air or other sustainable sources such as biomass fermentation and not from fossil fuels.

Generation of liquid fuels and their conversion to energy is currently not efficient and is economical only at large scale. To fully exploit the advantages of liquid fuels, it is therefore necessary to: (1) minimize production and conversion losses and make these processes scalable to small or medium sizes that match the scale of renewable generation; and (2) to use the existing infrastructure technologies, which is comprised of pipelines, railroads, tanker trucks, ships, terminals, as well as above- and below-ground storage. Developing technologies that work at a scale matching renewables generation and minimizing transportation/transmission and delivery costs creates opportunities for increased renewables deployment.

## C. PROGRAM OBJECTIVES

The overall objective of the **REFUEL** program is to develop novel, cost-effective technologies to create carbon-neutral liquid fuels (CNLFs) from water and air, using renewable electricity, and subsequently convert the CNLFs to power for transportation. If successful, the program outcomes will transform the way renewable electricity is stored and transported from remote generation sites to the end point customer. These changes will increase utilization of intermittent renewable energy and reduce carbon emissions.

The first specific objective of this FOA is to seek cost-effective and energy-efficient technologies for generation of energy-dense liquid fuels from renewable energy, water and air. These technologies should be scalable and match the scale of renewable energy generation, such as wind farms or solar arrays, and be tolerant to the uncertain and variable nature of renewable energy sources. For the purpose of this FOA, the appropriate scale for CNLF production is 150 MW of renewable energy, which matches a single mid-size solar/wind farm or combination of several renewable sources to increase the capacity factor. This size represents both scalability and compatibility with renewable resources. The resulting fuels should be transportable using liquid fuel infrastructure (already built or which can be built with known and already deployed technologies), and stored and dispensed as a liquid.

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<sup>48</sup> Meacham, J.R. et al., *J. Power Sources* (2006) 156, 472; Auld, A.E. et al., *IEEE Transactions on Energy Conversion* (2009) 24, 617.

<sup>49</sup> Melaina, M. and Eichman, J., "Hydrogen Energy Storage: Grid and Transportation Services", NREL report NREL/TP-5400-62518 (2015).



The second specific objective of this FOA is to develop efficient methods for the conversion of CNLFs to electricity or hydrogen (as an energy carrier for zero-emission vehicles). The only products of such conversion should be water and N<sub>2</sub> thus creating a net zero-carbon process; in the case of carbon containing fuels, CO<sub>2</sub> emissions are allowed as long as equal amounts are captured from air or other sustainable sources during the synthesis process.

The cost analysis needs to consider the entire value chain from generation through distribution to use. The cost targets for this FOA are selected in order to be disruptive with current state-of-the-art and be competitive with projected methods of electricity and hydrogen transmission, distribution, storage and delivery. The cost metric includes costs of fuel production, transportation, storage, and conversion to electricity or hydrogen. A 750 mile transportation scenario is used in this FOA, which is similar to a TransWest Express, LLC project to deliver the wind power from Wyoming to California.<sup>50</sup> The proposed technologies should demonstrate the potential to achieve the cost of **source-to-use delivered energy of below \$0.3/kWh** to the end value is based on the analysis of cost structure for projected large scale fuel manufacturing processes using renewable energy and known conversion processes, such as ICE or fuel cell power generation. The parameters for the analysis are presented in Table 3. An illustrative example of the cost structure of **source-to-use delivered** energy (including production, transmission, storage and conversion costs) for carbon- and nitrogen-based CNLFs compared to *projected* hydrogen vehicles and battery-electric vehicles (BEV) pathways is given in Figure 2 (cost assumptions are based on Table 3). If successful, the CNLF route will be more economical compared to other methods. The cost reduction potential for CNLFs and hydrogen comes from improving the production and conversion efficiencies (Figure 2), while for BEVs the battery cost is critical.

Only approximate calculations of the source-to-use delivered energy cost is required for the concept paper (CP) phase. Meeting or exceeding this target for small to medium scale processes is a great challenge, and can be addressed by improvements in fuel production or conversion or both. The ideal program outcome would be a suite of technology solutions that enable significantly reduced CO<sub>2</sub> emissions for transportation and increased penetration of renewables.

**Table 3:** Parameters for evaluation of the full costs of delivering transportation power using carbon-free energy sources.

Scenario	Synthetic (carbon-neutral) Gasoline	Carbon free H <sub>2</sub>	Carbon free NH <sub>3</sub>	Renewable electricity
Fuel production cost, \$/kWh	0.090 <sup>a</sup>	0.090 <sup>b</sup>	0.128 <sup>c</sup>	0.056 <sup>d</sup>
Transportation or transmission cost, \$/kWh <sup>e</sup> ,	0.001	0.060	0.004	0.038
Storage cost, \$/kWh <sup>e</sup>	0.001	0.030	0.008	0.106 <sup>f</sup>
Conversion efficiency, % <sup>e</sup>	30	55	55	92
Source-to-use energy cost, \$/kWh	0.303	0.327	0.256	0.236

<sup>a</sup> – Target \$3/gge set by EERE Office of Biotechnology and this FOA:

[http://energy.gov/sites/prod/files/2016/03/f30/At\\_A\\_GLANCE%20\(BETO\).pdf](http://energy.gov/sites/prod/files/2016/03/f30/At_A_GLANCE%20(BETO).pdf)

<sup>b</sup> – Target \$3/gge set by EERE Fuel Cell Technology Office; FCTO Multi-Year Research, Development, and Demonstration Plan, 3.1 Hydrogen Production (2015) [http://energy.gov/sites/prod/files/2015/06/f23/fcto\\_myrdp\\_production.pdf](http://energy.gov/sites/prod/files/2015/06/f23/fcto_myrdp_production.pdf)

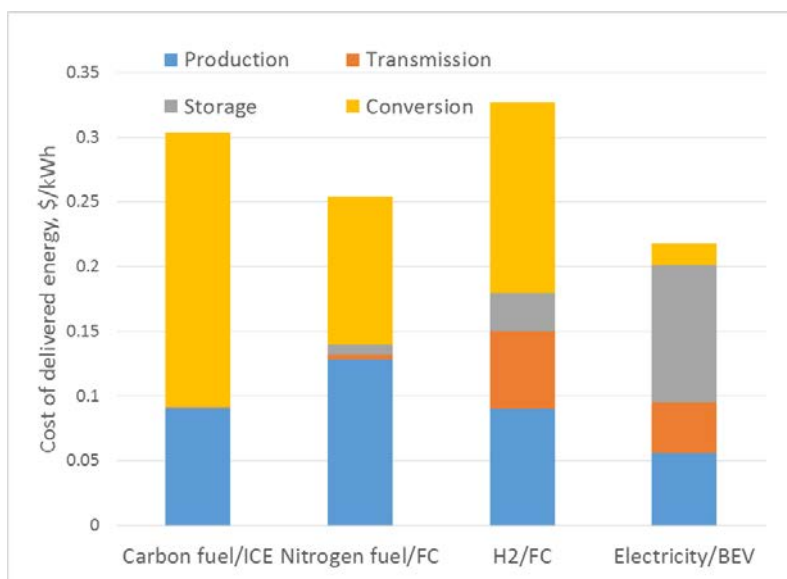
<sup>c</sup> – Target of this FOA.

<sup>d</sup> – Production cost for the solar:wind=60:40 mix from International Renewable Energy Agency (IRENA) (2015). “Renewable Power Generation Costs in 2014”, [http://www.irena.org/DocumentDownloads/Publications/IRENA\\_RE\\_Power\\_Costs\\_2014\\_report.pdf](http://www.irena.org/DocumentDownloads/Publications/IRENA_RE_Power_Costs_2014_report.pdf)

<sup>e</sup> – See Table 1 footnotes for assumptions.

<sup>f</sup> – Assumed battery pack cost \$200/kWh

<sup>50</sup> <http://www.powercompanyofwyoming.com/about/docs/The-Anschutz-Corporation-Overview.pdf>



**Figure 2. An example of the cost structure of source-to-use delivered energy for different pathways of renewable energy delivery.<sup>51</sup>**

Beyond the specific objectives of the individual program categories, an additional objective of the **REFUEL** program is to create a research community, from various backgrounds and disciplines, united by the common theme of enabling widespread integration of renewable energy via the use of energy-dense liquid fuels. The fuels research is often conducted with a focus on either production or conversion. ARPA-E seeks to advance a research and development agenda in which *both* sides are considered and optimized to enable innovation in this area.

## D. TECHNICAL CATEGORIES OF INTEREST

This program is focused on supporting chemistry and system concepts in energy transmission using CNLFs in one or both of the following categories:

- **CATEGORY 1: Small- and medium-scale synthesis of energy-dense carbon-neutral liquid fuels using water, air, and renewable energy source**
- **CATEGORY 2: Electrochemical processes for generation of hydrogen or electricity from energy-dense carbon-neutral liquid fuels**

The full impact of the **REFUEL** program will only be realized by linking these two categories and therefore *ARPA-E strongly encourages applications that address both categories*. For example, if proposing electrochemical production of a fuel, it is encouraged to also propose the electrochemical conversion of that fuel to electricity or hydrogen. Importantly, applications in Category 1 proposing the synthesis of a novel fuel for which there is no commercially accepted method for manufacturing and conversion to electricity or hydrogen are strongly encouraged to also propose an approach for the conversion of that fuel to electricity or hydrogen, i.e. must address both Category 1 and Category 2. If only Category 1 is proposed in this case, the Applicant must provide a reasonable explanation of how a conversion process for the fuel could be developed.

### Category 1:

The final deliverable for Category 1 is a laboratory prototype that can be scaled to a cost-competitive small- to medium-scale synthesis of energy-dense CNLFs using air, water, and renewable power such as wind and solar. Some possible CNLFs are commercially available (e.g. ammonia) and are produced over thousands of tons per year using thermochemical methods. In this program, production using new approaches based on the use of renewable energy as well as novel fuels or fuel compositions may be developed. All CNLFs have to be responsive to this FOA in the terms of physical properties,

<sup>51</sup> The parameters used for the source-to-use cost calculation are presented in Table 3.

energy density, handling, and conversion to electricity and fuels as defined in the technical targets section and metrics tables below. For example, a proposed fuel should be liquid over a practical range of temperatures, stable for an indefinite period of time, and compatible with existing methods and infrastructure for liquid storage and transportation. The required purity of fuels depends on the fuel type as well as on the application and this metric has to be defined by an Applicant and expressed in terms of content of the main component and the maximum concentration of individual impurities that have or may have a deleterious effect on the fuel use. A proposed fuel must have a high autoignition point (>200 °C) to ensure its safe use.

The synthesis of energy-dense CNLFs must be economical at small- to medium-scales to match the deployment of renewable power generation. This scale will require new methods to synthesize energy-dense fuels and innovative designs of chemical (**Subcategory 1A**) or electrochemical (**Subcategory 1B**) reactors. The current thermochemical production scale, e.g. Haber-Bosch synthesis of ammonia, is too large for the deployable scale of renewables (from 1 – 2 MW to 100 – 150 MW). The conventional process scales down poorly: the production cost increases from \$325/ton NH<sub>3</sub> (at the natural gas price \$5/MMBtu) for the production scale of 516,000 ton/year to \$545 to \$983 with decreasing the scale to 50,000 to 3,400 tons per year.<sup>52</sup> To match the capacity of the majority of new renewable energy installations (ca. 80 – 350 MW with average size of 90 MW (in 2009) for wind farms and 150 MW for solar PV plants),<sup>53</sup> fuel production plants should be a capable of generating around 10 – 25 ton NH<sub>3</sub>/hr at peak power with demonstrated energy consumption (Table 1). This scale is substantially smaller than a typical Haber-Bosch plant, which generates 50 – 125 ton NH<sub>3</sub>/hr in steady state,<sup>54</sup> and therefore represents a substantial challenge.

The production method should also be tolerant to intermittent energy supply, i.e. it should effectively operate at variable rates of production. For both existing commercial and newly-proposed fuels, both new synthetic methods and improvements to existing synthetic methods will be considered. Proposed synthetic methods must lead to a reduction of energy consumption and/or production cost. The proposed manufacturing methods may include known processes, e.g. intermediate hydrogen production by water electrolysis, though direct, one-pot synthetic methods are preferable. Only direct electrochemical conversion of CO<sub>2</sub> to CNLFs that can be directly used in fuel cells or in ICEs will be considered (**Subcategory 1B**).

The production cost for the proposed technology should be calculated using the input electricity price of \$0.05/kWh. For Applicants solely addressing Category 1, the total cost of delivered energy should be calculated using documented costs for fuel storage, transportation, and proposed use. For the concept paper, reasonable approximate values, as provided in Table 3, may be used. Input and output energy values should be used to calculate overall efficiency.

Examples of technical approaches include but are not limited to:

- High energy density fuels – Areas of particular interest are nitrogen-based fuels, e.g. ammonia, hydrazine hydrate and its derivatives including scaling down an air separation process; carbon containing fuels based on CO<sub>2</sub> capture from air or other sustainable sources thus enabling zero-carbon cycle, e.g. hydrocarbons or stable, non-corrosive oxygenates that can be used as a fuel for ICEs or fuel cells and be produced by direct electrochemical or thermochemical (one-pot) reaction.
- Novel methods for synthesis of known energy-dense liquid fuels – Areas of particular interests are direct electrochemical and thermochemical methods for synthesizing CNLFs that use water as a hydrogen sources instead of molecular hydrogen, and effective catalytic methods for hydrogen generation that allow for substantial decrease of operating pressures and temperatures.
- Innovative design of electrochemical and catalytic reactors operating at moderate pressure and temperatures and providing high yield per pass/volume and selectivity; membrane reactors that allow removal or supply of reactants thus shifting the equilibrium.
- Catalysts, electrocatalysts and materials to enable fuel synthesis.

<sup>52</sup>Maung, T. et al., “Economics of Using Flared vs. Conventional Natural Gas to Produce Nitrogen Fertilizer: A Feasibility Analysis”, North Dakota State University (2012): <http://purl.umn.edu/133410>

<sup>53</sup>Wiser, R., Bolinger, M., “Wind Technologies Market Report”, LBNL (2015), <https://ilsr.org/us-wind-projects-get-bigger-building-not-adding-turbines>

<sup>54</sup>Giddey, S., et al, *Int. J. Hydrogen Energy* (2013) 38, 14576.

## Category 2:

The final deliverable for Category 2 is a prototype that demonstrates efficient and cost-effective technologies for conversion of CNLFs to hydrogen to be used in H<sub>2</sub> refueling stations (*Subcategory 2A*) or directly to electricity for mobile applications (*Subcategory 2B*). The prototype must be scalable to an economically viable conversion for use in light, medium and heavy duty vehicles.

In ***Subcategory 2A***, to enable hydrogen refueling stations, it is necessary to generate hydrogen from a CNLF on demand with high yield and sufficient purity for use in commercial PEM fuel cells. Storing hydrogen in the form of a liquid fuel with hydrogen density greater than liquid hydrogen will reduce the cost and footprint of current hydrogen storage. CNLF decomposition that occurs at lower temperatures could decrease energy requirements for decomposition and enable smaller heat exchangers, leading to lower system costs. To achieve this goal, it is necessary to develop more active and less expensive catalysts. Delivery of H<sub>2</sub> at an elevated pressure will reduce the energy spent on compression. Development of modular system designs, e.g. several modules comprising smaller cracking reactors and compressors, could potentially greatly improve reliability of the refueling stations.

Direct conversion of CNLFs to electricity is the subject of ***Subcategory 2B***. Liquid fuels (e.g. methanol, NH<sub>3</sub>) can be used in low temperature (PEM, alkaline exchange membrane (AEM)) and high temperature (SOFC) fuel cells. Although the use of such fuels in fuel cells is well known, current technologies have low conversion and selectivity and are expensive. One of the major problems is the lack of active, selective and inexpensive electrocatalyst for anode reactions that limits current density and efficiency, and increases the stack cost. One possible solution is reforming (internal fuel cracking) to hydrogen, which is easier to oxidize. Another problem to be addressed is insufficient membrane conductivity leading to low power and therefore oversized stack cost, and, for low temperature fuel cells, low selectivity causing fuel crossover and reducing the fuel cell efficiency. Crossover is less pronounced for AEMs but they have the additional issue of low thermal stability. All types of fuel cells have the shared problem of sluggish kinetics for the oxygen reduction reaction (ORR) at the cathode, which is more pronounced for PEM FCs with acidic membranes and is less problematic for AEM fuel cells. In addition to development of more effective anode electrocatalysts and membranes, substantial improvements may be reached via novel electrode and cell design and better system integration. A separate ARPA-E program, Integration and Optimization of Novel Ion Conducting Solids (IONICS), has one Technical Category focusing exclusively on ex-situ testing of AEMs. In the IONICS program full cells will not be made and tested. In **REFUEL**, however, submissions to *Subcategory 2B* must propose full cells that meet the metrics defined below.

For Applicants solely addressing Category 2, the total cost of delivered energy should be calculated using documented costs for the carbon-neutral generation (using renewable energy), storage, and transportation of the fuels to be used. Input and output energy values should be used to calculate overall efficiency.

Examples of technical approaches for Category 2 include but are not limited to:

- High and intermediate temperature fuel cells for electricity generation directly from CNLF's – Areas of particular interest are approaches to novel, high power density electrode architectures; oxygen- or proton-conducting solid electrolytes; direct use of liquid fuels without ex-situ reforming; using non-platinum group metal catalysts; materials and device designs for long life fuel-air systems; integrated systems for combined heat and power generation.
- Ambient temperature fuel cells for electricity generation directly from CNLF's – Areas of particular interest are approaches to novel high power density membrane-electrode assemblies using anion exchange membranes; direct use of liquid fuels without reforming; using non-platinum group metal catalysts; system integration.
- Hydrogen generation systems for hydrogen refueling stations – Areas of particular interest are approaches to low temperature thermal catalytic cracking; electrochemical decomposition; high pressure delivery, electrochemical hydrogen compression.

The ideal project team will have engineering and scientific expertise in every aspect of the fuel production and/or conversion system design and a good understanding of catalysis, electrochemistry, material properties, energy storage systems, and catalytic or electrochemical reactor design. This teaming arrangement is especially important for projects focused on novel fuels because any claim of potential benefit requires a thorough understanding of their possible use for electricity or hydrogen generation and system design requirements. The team needs to have the necessary expertise in fuel and fuel cell manufacturing, though ARPA-E does not require the participation of the established industrial manufacturers.)



## E. TECHNICAL PERFORMANCE TARGETS

Proposed technical plans must show a well **REFUEL** realistic cost targets for source-to-use energy or hydrogen. To achieve this goal, the detailed Technical Performance Targets described below should be met. If an Applicant applies for both Categories 1 and 2, then some trade-offs between Category Technical Performance Targets for different process efficiencies may be considered. The final research objective for projects funded under this FOA is a fully functional prototype, specific for each subcategory (see Tables below), that credibly demonstrates all technical targets. The minimum prototype size, which is different for each subcategory, has been chosen by ARPA-E so that the results from the performance tests, as defined below, can be readily used to predict the performance, life-time, and cost of the proposed systems.

The cost of *source-to-use* electrical energy (in \$/kWh) is defined as the sum of CNLF production (technologies described in Category 1), transportation, storage, and conversion to electricity (technologies described in Category 2). *A clear justification of the potential to deliver a total cost of source-to-use energy below \$0.3/kWh must be provided for the application to be considered.* The scale of fuel production plant for this cost estimation should be 150MW. It is anticipated that several technical approaches are capable of meeting this target, and preference will be given to submissions that have demonstrated a potential to be substantially lower in the cost. Specific technical targets presented below are set to ensure that the overall vision may be realized and should be addressed in the application.

Concept Papers must include evaluation of the source-to-use delivered energy cost. If applying only to Category 1 then the Applicant should use literature values for cost of conversion technologies appropriate to the proposed fuel. If applying only to Category 2, then the Applicant should use literature values for the carbon-free production cost of the input fuel. *For simplicity, in the Concept Paper phase, transmission and storage costs for the calculation should be assumed to be \$0.02/kWh for any CNLF.* A more detailed cost calculation with references and stated assumptions will be required in the Full Application phase, at which point additional guidance will be provided. All proposed technologies have to be nearly zero-carbon, e.g. release no more than 50 g CO<sub>2</sub> from auxiliary processes per kWh produced energy.

### SUE Cost Estimation for Full Applications

Full Applications must include detailed estimation of the source-to-use delivered energy cost. The results must be presented in a Cost Analysis Workbook and in the technical volume (explain the SUE Cost Calculation provide a screenshot of the summary Cost Calculation spreadsheet tab). If applying only to Category 1 then the Applicant should use literature values for cost of conversion technologies appropriate to the proposed fuel. If applying only to Category 2, then the Applicant should use literature values for the carbon-free production cost of the input fuel. All proposed technologies must be nearly zero-carbon, e.g. release no more than 50 g CO<sub>2</sub> from auxiliary processes per kWh produced energy.

The following example values can be used in calculation of the SUE cost: If the proposed technology does not include the capturing feedstock from air, the feedstock cost should be assumed as \$40/ton for N<sub>2</sub><sup>55</sup> and \$250/ton for CO<sub>2</sub>.<sup>56</sup> Energy input required for H<sub>2</sub> production by water electrolysis by current technologies should be assumed as 49.2 kWh/kg H<sub>2</sub>.<sup>57</sup> For fuel production technologies, a lifetime of 25 years must be assumed, with a capacity factor of 32.5% for wind, 28.6% for PV solar, and 22.7% for thermal solar.<sup>58</sup> For conversion technologies, a lifetime of 15 years must be assumed, with a capacity factor of 65%, assuming the storage tanks can be appropriately oversized to supply continuous fuel input. Fuel transportation cost (CT) must be calculated based on the value of \$0.053/L for CNLF liquid at ambient conditions and \$0.057/L for liquefied gases. Fuel storage cost (CS) must be calculated based on the value of \$0.0026/L for CNLF liquid at ambient conditions and \$0.061/L for liquefied gases.<sup>59</sup> Unless a part of developing technology, the cost of electrochemical cell systems should be assumed as \$1600/kW for low temperature systems and \$1700/kW for high temperature systems

<sup>55</sup> <http://adgastech.com/Products/Industrial-Gas-Generators/Nitrogen-Generators/>

<sup>56</sup> Carbon Engineering, 2011

(<https://static1.squarespace.com/static/51957744e4b088893b86e2f3/t/51b228f9e4b0d25a229e7ca4/1370630392913/CE-Air-Capture-FAQ.pdf>)

<sup>57</sup> [https://www.hydrogen.energy.gov/pdfs/14004\\_h2\\_production\\_cost\\_pem\\_electrolysis.pdf](https://www.hydrogen.energy.gov/pdfs/14004_h2_production_cost_pem_electrolysis.pdf)

<sup>58</sup> [https://www.eia.gov/electricity/monthly/epm\\_table\\_grapher.cfm?t=epmt\\_6\\_07\\_b](https://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epmt_6_07_b)

<sup>59</sup> [https://www.iea.org/publications/freepublications/publication/FeaturedInsights/AlternativeFuel\\_FINAL.pdf](https://www.iea.org/publications/freepublications/publication/FeaturedInsights/AlternativeFuel_FINAL.pdf); Bartels, J. R., "A feasibility study of implementing an Ammonia Economy" (2008). Iowa State University, Graduate Theses and Dissertations. Paper 11132.

at power density of 410 mW/cm<sup>2</sup> and 290 mW/cm<sup>2</sup> respectively.<sup>60</sup> If the proposed technology requires different values than those stated above, Applicants must mark the related cells in color and provide suitable references to justify.

Applicants are strongly encouraged to use the REFUEL Cost Analysis Workbook, which is intended to serve as a template for the Applicant to detail the experimental evidence, literature references, and calculations used to determine the proposed cost of source-to-use energy at scale (in \$/kWh). For illustration purposes only, the Workbook is provided containing data for ammonia CNLF, which the Applicants should replace with data specific to their proposed technologies.

Whether or not Applicants choose to use the Workbook, Applicants must provide their team name, the fuel they are developing or using and its energy density, costs of fuel production, transportation, storage and conversion on a summary page. Applicants must also enter data for implementing the proposed technology at scale of 150 MW of input energy. Hydrogen production cost (Subcategory 2a) must be calculated for 1000 kg/day scale. If there is no available data on SUE cost components the Applicant is expected to provide literature data (marked in color) or describe the assumptions made to generate the cost metrics and provide any calculations in a separate spreadsheet tab. Use of built-in Microsoft Excel functions are acceptable, however, add-in functions or software not provided with OEM Microsoft Excel installations are not permitted. When experimental or reference values are provided, clearly notate the source and relevant assumptions.

### Category 1:

The following metrics apply to all projects in Category 1 (see subcategory targets for additional metrics):

ID	Description	Target
1.1	Fuel cost on primary energy basis at 150MW scale	< \$0.13/kWh
1.2	Fuel energy density	> 3.5 kWh/L
1.3	Storage temperature	above -40°C <sup>1</sup>
1.4	Storage pressure	below 20 bar <sup>2</sup>
1.5	Autoignition point	> 200 °C
1.6	Liquid fuel viscosity	< 100 Centipoise
1.7	CO <sub>2</sub> released in fuel production	< 50g CO <sub>2</sub> /kWh of fuel energy content

<sup>1</sup> – at ambient pressure

<sup>2</sup> – at ambient temperature

*Subcategory 1A* is comprised of chemical (catalytic) synthesis of energy-dense CNLFs based on hydrogen produced from water splitting and innovative designs of chemical reactors. The following metrics apply to projects in subcategory 1A:

Specific to subcategory 1A: Chemical production		
ID	Description	Target
1A.1	Reaction rate	> 7x10 <sup>-7</sup> mol cm <sup>-2</sup> s <sup>-1</sup>
1A.2	Final prototype productivity	> 1 kg CNLF/day
1A.3	Total production energy efficiency	> 60%
1A.5	Fuel synthesis efficiency	> 86%
1A.6	Fuel purity	> 99%

*Subcategory 1B* is comprised of electrochemical and thermochemical synthesis of energy-dense CNLFs using water and innovative designs of electrochemical reactors and thermochemical systems. The following metrics apply to projects in subcategory 1B:

<sup>60</sup> James, B.D. and DeSantis D.A. "Manufacturing Cost and Installed Price Analysis of Stationary Fuel Cell Systems"

(<https://www.sainc.com/service/SA%202015%20Manufacturing%20Cost%20and%20Installed%20Price%20of%20Stationary%20Fuel%20Cell%20Systems.pdf>)

Specific to subcategory 1B: Electrochemical production		
ID	Description	Target
1B.1	Current density for electrochemical production	> 300 mA/cm <sup>2</sup>
1B.2	Final prototype productivity	> 100 g CNLF/day
1B.3	Coulombic efficiency	> 90%
1B.4	Production energy efficiency	> 60%
1B.5	Degradation rate	0.3%/1000 hrs
1B.6	Fuel purity	> 99%

End-of-project deliverables:

Both subcategories have to deliver a detailed techno-economic analysis based on a comprehensive model meeting all of the technical targets and demonstrate a pathway to the CNLF cost target at a scale of 150 MW input energy.

Subcategory 1A: Demonstration of a bench scale reactor producing a CNLF at >1 kilogram per day.

Subcategory 1B: Demonstration of a short stack prototype producing a CNLF at >100 gram per day.

*Any application proposing the synthesis of a novel fuel for which there is no commercially accepted method for manufacturing should indicate a technical path and use reasonable conversion cost for conversion to electricity or hydrogen. In this case Applicants are strongly encouraged to submit to Categories 1 and 2 and to meet all relevant metrics.*

Supplemental Explanation of Category 1 Performance Targets:

**1.1** See the full explanation in the overview of this Section.

**1A.1** Proposed manufacturing process of a CNLF should be tolerant to intermittent nature of renewables. The process should be demonstrated with a prototype reactor at a kg/day scale in a continuous (500 hours) operation with at least 5 interruptions designed to test the effect of intermittency in power supply.

**1A.3** Total production energy efficiency is defined as the ratio of CNLF primary energy to total consumed energy when water is used as hydrogen source.

**1A.4** Fuel synthesis efficiency is defined as the ratio of primary energy to consumed energy when a CNLF is synthesized using hydrogen.

**1B.1** Proposed manufacturing process of a CNLF should be tolerant to intermittent nature of renewables. The process should be demonstrated with a prototype reactor at a kg/day scale that operates for 500 hours continuously with at least 5 on/off cycles.

**1B.4** Production efficiency is defined as the ratio of theoretical process energy to consumed energy.

**1B.5** Degradation is defined as the increase in cell voltage at the target current density.

**Category 2:**

Subcategory 2A is comprised of hydrogen generation from CNLFs using thermal or electrochemical pathways and innovative reactor design. The following metrics apply to projects in subcategory 2A:

Subcategory 2A: Hydrogen generation		
ID	Description	Target
2A.1	Hydrogen delivered cost at target pressure	< \$4.5/kg
2A.2	Final prototype size	10 L H <sub>2</sub> /min
2A.3	Hydrogen generation rate	> 0.15 g H <sub>2</sub> /h/cm <sup>3</sup>
2A.4	Conversion to hydrogen	> 99%
2A.5	Energy efficiency	> 80%
2A.6	Maximum cracking reactor temperature	450 °C
2A.7	Hydrogen delivered pressure	30 bar
2A.8	Life time (projected)	10 yrs
2A.9	Concentration of catalyst poisoning impurities	< 100 ppb

Subcategory 2B is comprised of electricity generation from CNLFs using electrochemical fuel cells and innovative cell design. The following metrics apply to projects in subcategory 2B:

Subcategory 2B: Direct use of fuel		
ID	Description	Target <sup>a</sup>
2B.1	Delivered source-to-use energy cost target	< \$0.3/kWh
2B.2	Final prototype size	50 W
2B.3	Maximum operating temperature	650 °C
2B.4	Current density at 0.75 V	> 300 mA/cm <sup>2</sup>
2B.5	Electrical efficiency@ 25% of rated power	> 55%
2B.6	Minimum continuous stack testing time	500 hours
2B.7	Power degradation rate	< 0.3% per 1,000 hours

<sup>a</sup> – For more guidance on system requirements see DOE Fuel Cell Technical Team Roadmap (2013), [http://energy.gov/sites/prod/files/2014/02/f8/fctt\\_roadmap\\_june2013.pdf](http://energy.gov/sites/prod/files/2014/02/f8/fctt_roadmap_june2013.pdf) (mobile applications) and DOE Solid State Energy Conversion Alliance (SECA) program, <http://www.netl.doe.gov/research/on-site-research/research-portfolio/coal-research/seca-index> (stationary applications)

End-of-project deliverables:

Both subcategories have to deliver a detailed techno-economic analysis based on a comprehensive model meeting all of the targets.

*Subcategory 2A:* Demonstration of a bench scale cracking reactor or electrochemical cell stack producing H<sub>2</sub> from a CNLF at greater than 100 grams per day.

*Subcategory 2B:* Demonstration of a short stack prototype of at least 50 W and consisting of at least 3 cells with a total working area greater than 250 cm<sup>2</sup>. The fuel must be fed directly to the anode; concepts that propose an external fuel processing unit will not be considered for selection.

Supplemental Explanation of Category 2 Performance Targets:

- 2A.1 See the full explanation in the overview of the Technical Targets section.
- 2A.3 Conversion to hydrogen is defined as the percentage of extracted hydrogen from containing in a CNLF.
- 2A.4 Energy efficiency (EE) is defined as  $EE = P/(P+E)$  where  $P$  is the primary energy of extracted hydrogen and  $E$  is energy consumed for the conversion process.
- 2A.7 Testing time for the projects will be 500 hours.
- 2A.8 Concentration of ammonia or other fuel cell catalyst poisoning gases in generated hydrogen should be less than 100 ppb for its direct use in a PEM fuel cell.
- 2B.1 See the full explanation in the overview of the Technical Targets section.
- 2B.5 Electrical efficiency is defined as the ratio of produced electrical energy to primary energy of a CNLF.
- 2B.7 Degradation is defined as the decrease in fuel cell voltage at the target current density