

# Sustainable Mobility, Future Fuels, and the Periodic Table

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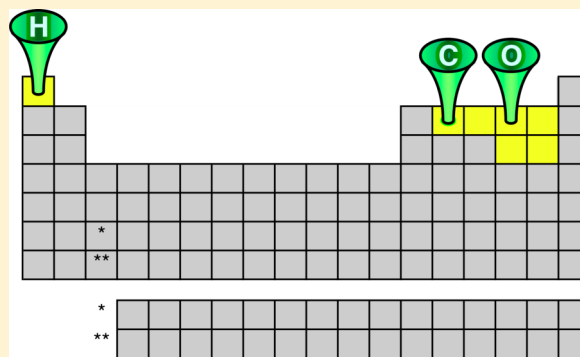
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## S Supporting Information

**ABSTRACT:** Providing sustainable mobility is a major challenge that will require new vehicle and fuel technologies. Alternative and future fuels are the subject of considerable research and public interest. A simple approach is presented that can be used in science education lectures at the high school or undergraduate level to provide students with an understanding of the elemental composition of future fuels. Starting from key fuel requirements and overlaying the chemical trends evident in the periodic table, it can be demonstrated that future chemical fuels will be based on three elements: carbon, hydrogen, and oxygen. Liquid hydrocarbons are the most convenient transportation fuels because of their physical state (easier to handle than gases or solids) and their high gravimetric and volumetric energy densities. Challenges remain for storage of electricity and gaseous fuels. Recognizing the need to address climate change driven by increasing emissions of CO<sub>2</sub>, sustainable mobility will be powered by low-CO<sub>2</sub> hydrogen, low-CO<sub>2</sub> hydrocarbons, low-CO<sub>2</sub> oxygenates, low-CO<sub>2</sub> electricity, or a combination of the above.

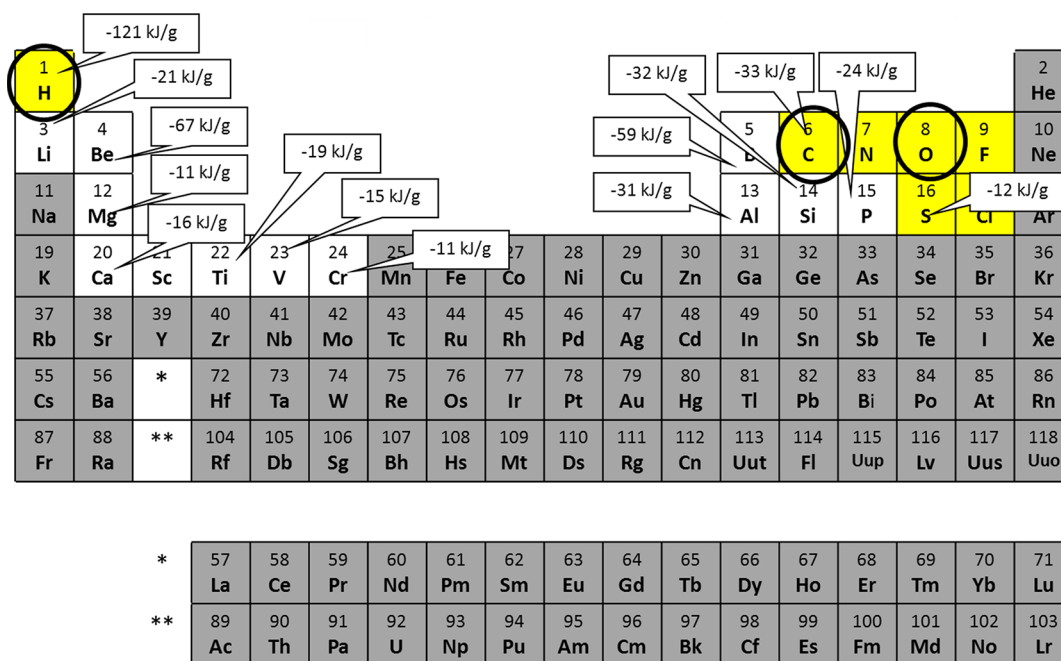


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Climate change and energy security are long-term challenges. From an energy security viewpoint, the United States (U.S.) is fortunate in having large reserves of coal (approximately 240 years of supply at the current rate of production<sup>1</sup>) and natural gas (technically recoverable resources including shale gas deposits are equivalent to approximately 100 years of supply at the current rate of production<sup>2</sup>). However, approximately 94% of the U.S. transportation energy demand is supplied by petroleum.<sup>3</sup> U.S. reserves of petroleum are limited and domestic production has fallen from a peak of 11.3 million barrels per day in 1970 to 6.8 million barrels per day in 2006.<sup>1</sup> (Recently, the decline in U.S. oil production has been halted and production has increased to 7.9 million barrels per day in 2011.) Despite the decline in domestic production, over the period 1970–2011, the consumption of oil in the U.S. has increased from 14.7 to 18.8 million barrels per day<sup>1</sup> and the fraction of oil demand that is met by imported oil has increased from approximately 20% to 60%, albeit down from 66% in 2005–2006. The nearly complete dependence of a vital economic sector on a limited domestic energy resource is clearly a source of concern.

Climate change is caused by increasing levels of greenhouse gases in the earth's atmosphere resulting from human activities.<sup>4</sup> CO<sub>2</sub> released during fossil fuel combustion and deforestation is the largest contributor to radiative forcing of climate change.<sup>4</sup> Road transportation in the United States and EU-15 is responsible for approximately 5% and 4% of global fossil fuel CO<sub>2</sub> emissions, respectively.<sup>5</sup> On a global basis, in 2007, road transportation was responsible for approximately 5 gigaton (Gt) of global fossil fuel CO<sub>2</sub> emissions,<sup>6</sup> which represents about 17% of the approximately 30 Gt total global CO<sub>2</sub> emissions. The United Nations Framework Convention on Climate Change<sup>7</sup> has been ratified by 192 countries and calls for stabilization of greenhouse gas concentrations in the atmosphere at a level that would "prevent dangerous anthropogenic interference with the climate system". Although there is no consensus on a precise level of CO<sub>2</sub> in the atmosphere that would prevent such interference, levels in the range 350–550 parts per million (ppm) are typically discussed.

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**Figure 1.** Elements with enthalpy of oxidation greater than 10 kJ/g are labeled with caption boxes. Elements with nonsolid oxides are indicated by yellow boxes. Circles highlight the elements left after eliminating elements with (i) solid oxides, (ii) low heat release on oxidation, and (iii) toxic oxides. Oxygen is included because oxygenates have combustion chemistry advantages in spark-ignited engines and are conveniently derived from biomass.

Meeting these targets will require the research, development, and deployment of new low-CO<sub>2</sub> vehicle and fuel technologies as well as CO<sub>2</sub> reductions from other sectors (e.g., heating and power production and industrial production processes). Reducing emissions by the amount consistent with climate stabilization requires partnership of all stakeholders, including the automotive industry, the fuel industry, government, and consumers and including public and private transportation modes.

In the following, a chemical perspective on sustainable mobility and future transportation fuels for use in chemical education is described (see the Supporting Information). We start with a discussion of the chemical and physical properties required for transportation fuels and then consider these requirements with respect to the trends evident in the periodic table. This analysis explains the dominance of hydrocarbon and, to a lesser extent, oxygenate hydrocarbon fuels in the current transportation system. We then discuss implications for future fuels. Our aim is to provide a teaching aid for use in discussions regarding future fuels and sustainability. Discussions of sustainable mobility should also include quantitative decisions on the transport of goods and persons (numbers, mass, speed, and distance regulations), which are beyond the scope of the present work. Finally, it should be noted that the term “low-CO<sub>2</sub>” refers to technologies with low fossil-carbon emissions. Current hydrocarbon fuels are produced from petroleum and are not sustainable. Future low-CO<sub>2</sub> fuels produced using nonfossil carbon and renewable energy sources are being investigated as sustainable fuels.<sup>8,9</sup> Teaching materials related to hydrogen as a future fuel and estimating CO<sub>2</sub> emissions from current vehicles are available<sup>10,11</sup> and could be used to supplement the analysis described below.

## PROPERTIES OF A TRANSPORTATION FUEL

The function of a transportation fuel is to provide the energy needed to move the vehicle and its passengers and cargo. Nearly all road transportation vehicles (cars, trucks, buses) are not connected directly to energy sources and hence need to carry their fuel on-board. Energy is released from the fuel as a result of chemical reactions. Reactants need to be stable under typical storage conditions (ambient temperature and pressure). Unimolecular reactions require an unstable reactant and are generally unsuited to provide energy for transportation for safety reasons. For vehicle applications, two reactants are required for the chemical reaction releasing energy. The on-board fuel is the first reactant. Recognizing the desire to avoid the complexity and added weight of an additional storage and handling system, there is a large incentive not to carry the second reactant on the vehicle. One case in point is common battery chemistries such as nickel–metal hydride (NiMH) and Li-ion, which contain two reactants (anode and cathode) and exhibit gravimetric energy densities that are significantly smaller than conventional liquid fuels. The atmosphere is a logical source for the second reactant. The atmosphere consists of approximately 78% N<sub>2</sub>, 21% O<sub>2</sub>, and 1% Ar. N<sub>2</sub> is a very poor reactant (the N≡N bond is too strong), Ar is unreactive, and this leaves O<sub>2</sub> as the choice for the second reactant.

Although there are many requirements that transportation fuels must fulfill, from a chemical perspective, only four key properties need to be considered that serve to define the required elemental composition of future fuels. First, the fuel should have a highly exothermic reaction with O<sub>2</sub> and release a substantial quantity of energy per kilogram of fuel (minimizing weight is critical for vehicle range and performance). Second, the fuel and its oxidation products (exhaust) should be easy to handle (i.e., liquid or gas, not solid, over the typical temperature operation range of −20 to +40 °C). One exception to this rule would be the subset of solids that could be efficiently reversed

on-board via electrochemical means, as done in rechargeable batteries. Third, the exhaust should be nontoxic and unreactive under ambient conditions. Fourth, the fuel should either be abundant in nature, or it should be easy to make, recycle, or regenerate; millions of tons are needed each day (current daily global oil consumption in transportation is approximately 6 million tons) and it should be available from environmentally benign and sustainable sources.

## ■ THE PERIODIC TABLE

The starting point in the search for optimal fuels is the periodic table. The periodic table is very familiar to chemists and presents the elements arranged according to their atomic structure and chemical properties. The future fuels used in transportation will be either elements in the periodic table or compounds made from elements. Some elements can mix in a continuous fashion (e.g., in alloys), and in principle, there are an unlimited number of possible compounds that can be made. At first it seems a daunting task to consider the vast number of compounds that are, in principle, available for potential use as fuels. However, the task is simplified dramatically with the help of the perspective gained from a consideration of trends in the periodic table. The first requirement is that the fuel must have a highly exothermic reaction with  $O_2$  (for batteries, the Gibbs energy of reaction is the most relevant descriptor, and thus, we address batteries separately). Compounds whose enthalpy of formation is positive are not abundant in nature, tend to be unstable and highly reactive, and are generally unsuitable as light-duty vehicle fuels (although they are used as rocket fuels, e.g., dimethylhydrazine). Hence, for the present purposes, the search is restricted to compounds with heats of formation that are negative. For such compounds, the maximum exothermicity of oxidation of the compound can be equated to the highest exothermicity of oxidation of the constituent elements. The energy released per unit mass generally decreases on moving down within a group in the periodic table, reflecting two trends: (i) the strength of the chemical interactions in forming the oxides within a group generally decreases as the mismatch between the size of the atoms in the lattice increases, and (ii) the mass of the element increases.

To satisfy the typical demands of range and performance, vehicles need to carry on-board a significant quantity of energy. The lower heating value of a fuel is the heat liberated on combustion to  $CO_2$  and water vapor. The lower heating value of gasoline, for example, is approximately 122 MJ per U.S. gal (32 MJ/L). To meet today's customer expectations, a light-duty vehicle typically needs to provide sufficient fuel capacity for a range of approximately 300–400 mi (480–640 km). Depending on the vehicle size and, hence, fuel economy, this requires the vehicle to carry 10–20 gal (40–80 L, 30–60 kg) of gasoline fuel, which equates to approximately 1–2 GJ of chemical energy. Recognizing that a new fuel may not be able to achieve the energy density of hydrocarbons, and the practical considerations associated with transferring a large mass of fuel at refueling, it is impractical to handle more than 100–200 kg of fuel. Hence, the fuel needs to liberate at least 10 kJ/g on oxidation. Figure 1 shows the elements satisfying this criterion. The available elements largely appear at the top of the periodic table. Figure 1 also shows the elements satisfying the second requirement that the fuel and its oxidation products should be easy to handle (i.e., not solids). Metal oxides are typically solids, and hence, elements that satisfy the requirement that the exhaust is not a solid are the nonmetals that are located toward

the right side of the periodic table. Using the third requirement to eliminate sulfur because it forms a toxic oxide gives the circled elements in Figure 1 that shows why hydrogen and carbon are key elements in transportation fuels.

Biofuels such as ethanol and biodiesel contain oxygen (ethanol is 35% oxygen by weight, biodiesel is approximately 10% oxygen by weight) and are commonly referred to as oxygenated hydrocarbons or simply oxygenates. Because these fuels are partially oxidized hydrocarbons, they release less energy upon combustion than their hydrocarbon counterparts on both a mass and volume basis. Thus, oxygen in a fuel is undesirable from an energy density standpoint. Nevertheless, the presence of oxygen in future fuels is likely because of several factors. First, biomass feedstocks contain oxygen (e.g., glucose:  $C_6H_{12}O_6$ ; cellulose is a glucose polymer:  $(C_6H_{10}O_5)_n$ ). Second, although transformation processes that convert biomass into biofuels generally target a reduction in oxygen content, it is not necessary or desirable to remove all of the oxygen because it can provide desirable properties for engines. The hydrogen bonding in liquid oxygenated fuels results in greater evaporative cooling when liquid fuel is sprayed into the engine, which decreases the likelihood of autoignition, increases the octane value of the fuel, and allows for more efficient combustion in spark-ignited engines.<sup>12</sup> Finally, the combustion of oxygenated fuels may lead to lower emissions of carbon monoxide, soot, and unburned hydrocarbons from some engines.

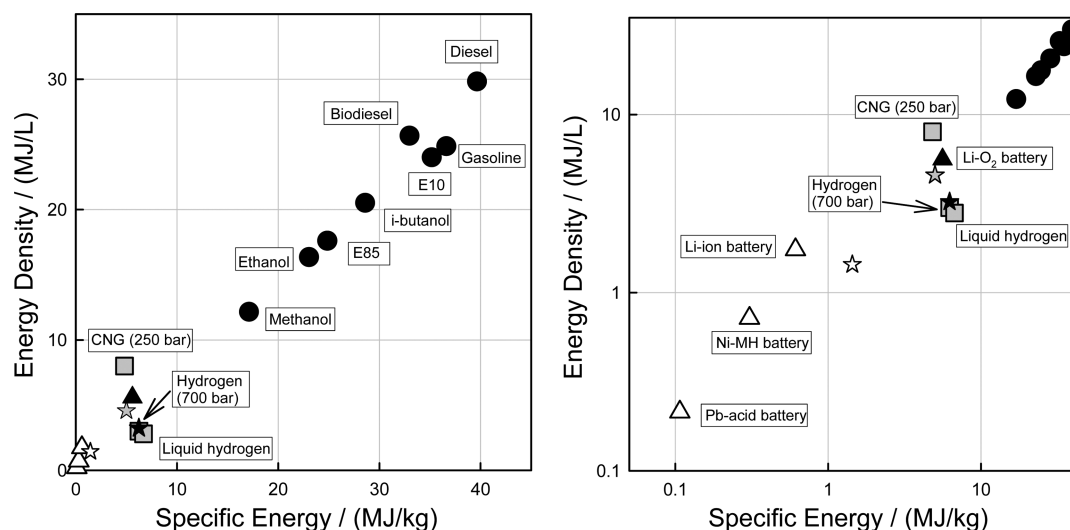
Other elements can be tolerated in fuels and may add desirable properties, but these are typically additives present in trace quantities to protect engine components. Sulfur compounds present in refined petroleum in parts per million levels increase the lubricity of the fuel, which tends to reduce engine wear. On the other hand, sulfur is a poison for catalysts used for tailpipe emissions control, and thus, sulfur levels in fuel have been reduced by regulations over time. Lubricity additives (used in ppm levels) may contain nitrogen in addition to carbon, hydrogen, and oxygen. Detergents are added in small quantities (ppm) to keep fuel systems clean and reduce engine deposits.

The analysis presented above provides a simple framework to explain the dominance of hydrocarbon and, to a lesser extent, oxygenated hydrocarbon fuels in the current transportation system and serves as a starting point for a discussion of future fuels.

## ■ FUTURE FUELS

The fuels that will be used in future transportation need to meet the requirements discussed in the previous section and be available at large scale from sustainable sources. Sustainability has three pillars: economic, social, and environmental. We will concentrate on the environmental pillar as a discussion of economic and social factors is beyond the scope of the present work. To address climate change, the life cycle greenhouse gas emissions associated with transportation (and all other sectors of the economy) need to be reduced substantially. For light-duty vehicles, hydrogen, hydrocarbon fuels, and electricity are possible fuels. In all cases, these fuels must provide low- $CO_2$  emissions including both the feedstock and fuel-production processes (e.g., electricity, hydrogen, or hydrocarbons generated from renewable sources such as wind, solar, or biomass).

Vehicle design constraints imply that energy density (MJ/L) and specific energy (MJ/kg) are important parameters for a fuel. The stored fuel takes up volume that would otherwise be usable for passengers or cargo and adds weight to the vehicle,



**Figure 2.** Energy density (MJ/L) and specific energy (MJ/kg) for selected fuels (includes both fuel and fuel storage system) on linear (left panel) and log scales (right panel). Circles are fuels that are liquid under ambient conditions. Squares are fuels that are gases under ambient conditions. Batteries are shown as triangles, with open triangles representing current battery chemistries (Li-ion, nickel–metal hydride, lead-acid) and the filled triangle representing the projected performance of a Li–O<sub>2</sub> “metal–air” battery. Solid hydrogen storage systems are shown as stars (open = complex metal hydrides, black = adsorbents, gray = chemical hydrides); see text for details.

which directly affects the vehicle fuel economy and performance. In addition to the fuel itself, engineers need to consider the volume and weight associated with the container needed to store the fuel. In the discussion below, the energy density and specific energy are considered for selected fuels and both the fuel and the fuel storage system were included in the calculations. For a liquid-fuel storage system (gasoline, diesel, ethanol, biodiesel), the volume and weight of the fuel storage system typically adds little mass and volume. However, for gaseous fuels and electricity, the storage system adds considerable mass and volume (see Figure 2).

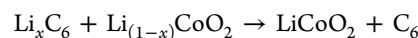
Energy densities of fuels typically reflect enthalpies of combustion also known as heating values. The higher values assume that all products are returned to the initial temperature (at 25 °C this value is the same as the enthalpy of combustion and includes the enthalpy of condensation of water), whereas the lower values assume water remains in the gaseous state (in practice subtracting the enthalpy of vaporization of any water produced). As most combustion processes used in transportation emit hot gaseous products, the lower values are typically used.

Hydrogen has a very high energy content, with a lower heating value of 121 MJ/kg of H<sub>2</sub>. However, there is currently considerable weight associated with on-board hydrogen storage (as reflected in the data in Figure 2). Hydrogen may be stored on-board a vehicle in several forms, including compressed gas, cryogenic liquid, and in solid-state form, the latter of which includes storage in complex metal hydrides, adsorbents, or chemical hydrides.<sup>13</sup> An example of a reversible hydrogen storage reaction involving the complex metal hydride sodium alanate (NaAlH<sub>4</sub>) is



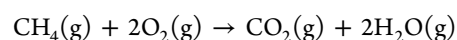
In this reaction, hydrogen can be liberated from the hydride by heating, potentially making use of waste heat from a fuel cell or internal combustion engine, while the process of refueling involves absorption of pressurized H<sub>2</sub> gas. Values for the energy densities of hydrogen storage systems are taken from Ahluwalia et al.<sup>14</sup>

Batteries are closed systems in which an applied potential is used to recharge the battery and thereby replenish its energy content. Consequently, batteries are unlike the other fuels considered here, as some form of mass transfer must occur to refuel those systems. The capacity of a battery is expressed in coulombs or ampere–hours and is an extensive quantity that depends upon the amount of active materials stored within the cell. The practical energy content of a battery can be determined by multiplying the observed discharge voltage by the capacity: volts × ampere–hours = watt–hours. Energy densities can then be evaluated by dividing by the mass or volume of the system. The theoretical specific energy of a battery is defined as the change in the Gibbs energy,  $\Delta G$ , associated with the discharge reaction divided by the masses of the active materials; this quantity is often used to compare battery chemistries. An example of a discharge reaction in a typical Li-ion cell is the intercalation of Li<sub>(1-x)</sub>CoO<sub>2</sub> to form LiCoO<sub>2</sub>:

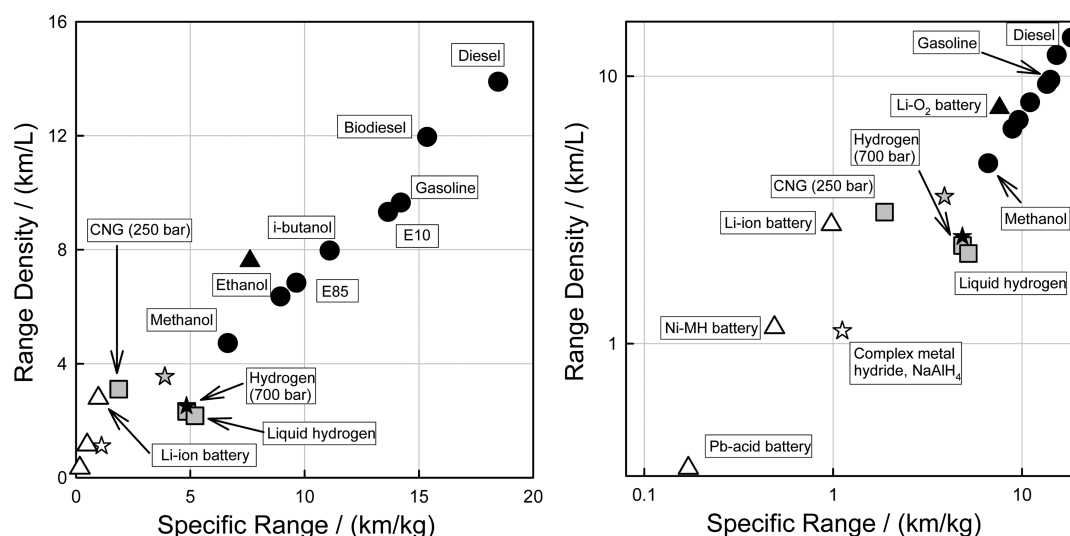


In the charged stage, Li predominately resides in the carbon-based anode (Li<sub>x</sub>C<sub>6</sub>) and during discharge migrates from the anode to the LiCoO<sub>2</sub>-based cathode. The energy densities in Figure 2 for three common rechargeable battery chemistries (lead-acid, nickel–metal hydride, and lithium-ion) are taken from Linden and Reddy.<sup>15</sup> The energy density for the Li–O<sub>2</sub> battery, which is a potential future battery chemistry with very high energy density, is taken from Christensen et al.<sup>16</sup>

For compressed natural gas (CNG) systems, Kramer and Anderson<sup>17</sup> have reported that typically 12–20 kg of CNG is stored on a vehicle, which usually enables a cruising range of 250–450 km (155–280 mi). The additional weight of the complete CNG system is approximately 150 kg, while the package space occupied by the fuel tanks is approximately 100 L. The composition of CNG varies depending on the source, but it is mostly methane. The combustion of methane is described as



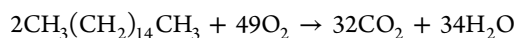
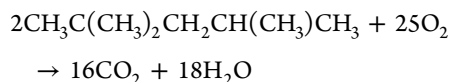




**Figure 3.** Volumetric (km/L) and gravimetric (km/kg) range densities for selected fuels (includes both fuel and fuel storage system) on linear (left panel) and log scales (right panel). Circles are fuels that are liquid under ambient conditions. Squares are fuels that are gases under ambient conditions. Batteries are shown as triangles. Solid hydrogen storage systems are shown as stars (open = complex metal hydrides, black = adsorbents, gray = chemical hydrides); see text for details.

and the lower heating value for methane is 50 MJ/kg.

Whereas gasoline and diesel are complex mixtures of hydrocarbons their oxidation chemistry can be represented by iso-octane [2,2,4-trimethylpentane,  $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$ ] and cetane (hexadecane,  $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$ ), respectively.



Lower heating values for gasoline, diesel, methanol, and ethanol of 43, 45.8, 20, and 26.9 MJ/kg, respectively, were taken from Heywood.<sup>18</sup>

In general, liquids are more easily stored than gases or electricity, and so the physical state of the fuel under ambient conditions is an important consideration. Figure 2 shows plots of energy density (MJ/L) versus specific energy (MJ/kg) for electricity [stored in Li-ion, nickel metal hydride (Ni-MH), lead acid (Pb-acid), or Li–O<sub>2</sub> batteries], hydrogen (cryogenic liquid, compressed gas, or in solid storage systems), methane (compressed gas), ethanol, *i*-butanol, gasoline, and diesel. The left and right-hand panels show the data on linear and log scales, respectively. It should be emphasized that the data in Figure 2 include both the fuel and the fuel storage system. For gaseous fuels, there can be a large impact from the fuel storage system on the specific energy. For example, hydrogen gas has a specific energy of 121 MJ/kg, but when packaged on a vehicle, hydrogen gas plus its 700 bar storage tank has a specific energy of 6.2 MJ/kg.<sup>14</sup> The low energy densities associated with storing electricity and gaseous fuels illustrate the challenges faced by these vehicles in comparison to conventional gasoline or diesel powered vehicles. The data for liquid fuels in Figure 2 fall along a line of slope 0.75 drawn through the origin. This behavior is explained by the fact that the fuel storage systems for liquid fuels add relatively little volume or mass. Hence, the ratio of energy density (MJ/L) to specific energy (MJ/kg) largely reflects the density (kg/L) of the liquid fuels. No such

simple correlations are evident for the gaseous fuels or batteries shown in Figure 2.

One important factor that is not captured in Figure 2 is the fact that electric and hydrogen fuel cell vehicles are inherently more energy efficient than their internal combustion engine counterparts. The efficiency of internal combustion engines is much lower than that of fuel cells and electric motors, and this will partially offset the advantage of high energy densities exhibited by liquid fuels. For similar levels of functionality, electric and hydrogen fuel cell vehicles use approximately 3.5 and 2 times less on-board energy,<sup>19</sup> respectively, per mile than their gasoline counterparts. Using the average fuel economy of 29.6 mi/gal for 2011 model year light-duty cars and trucks in the United States<sup>20</sup> and literature data<sup>19</sup> for the relative energy efficiencies of the different vehicle technologies gives the range density (km/L) and specific range (km/kg) values shown in Figure 3. Comparison of Figure 3 with Figure 2 shows that hydrogen and electricity (in Li-ion batteries) are significantly more competitive with liquid hydrocarbon fuels after accounting for the efficiency of the different vehicle technologies and helps explain the current interest in such vehicles. Even so, to achieve the typical 300 mi (480 km) range of today's vehicles, a battery electric vehicle or H<sub>2</sub>-fuel cell vehicle would require considerably more weight and volume for fuel storage than a liquid-fueled vehicle. Further advances in energy storage technologies, such as solid-state hydrogen storage materials<sup>13</sup> or metal–O<sub>2</sub> batteries,<sup>16</sup> could further close the gap between fuel cell and electric vehicles and their liquid-fueled counterparts shown in Figure 3.

## SUMMARY

Chemical trends in the periodic table and simple physics are used to explain the current dominance of liquid hydrocarbons as transportation fuels. It is shown that sustainable mobility will be powered by low-CO<sub>2</sub> hydrogen, low-CO<sub>2</sub> hydrocarbons, low-CO<sub>2</sub> oxygenates, low-CO<sub>2</sub> electricity, or a combination of the above. The analysis presented above may be useful in science education for global sustainability.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Material for a presentation. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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