Computer-aided search for materials to store natural gas for vehicles

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Abstract Most cars use gasoline as a fuel. But cars can run on other fuels, such as natural gas, the same gas that is used for cooking and heating in our homes. Natural gas is cheaper and possibly better for the environment than gasoline. To use natural gas in a car, we need to densify it so that we have enough gas in the fuel tank to drive a similar distance as with a tank of gasoline, which is a liquid where the molecules are already closely packed together. Current technologies compress natural gas to a pressure so high that we need expensive compression equipment and bulky, heavy, and expensive tanks that take up space in the trunk. As an alternative storage strategy, researchers are trying to find novel materials that act as sponges for natural gas. These sponges can adsorb natural gas so that we can achieve a similar density to compressed natural gas, but now with a lower pressure so that we can use lighter, cheaper tanks that are the same shape as gasoline tanks. Plus, with more affordable compression equipment, we could refill our fuel tanks at home with the same gas we use for cooking and heating. Interestingly, we can use computers to try to find such materials. What these computer studies show is that these sponge-like materials are not as promising as we had hoped; the very best sponge-like material cannot achieve a density of natural gas as high as compressed natural gas.

Most cars use gasoline as a fuel. But cars can run on other fuels, such as natural gas, the same gas that is used for cooking and heating in our homes. Natural gas is an attractive alternative fuel for vehicles. In the US, the domestic supply of natural gas is abundant, and the recent boom in "fracking", or more precisely, hydraulic fracturing and horizontal drilling, has enabled us to extract more of the natural gas trapped in deep, underground rock formations. This abundant supply makes natural gas relatively cheap. There are many discussions about the impact of fracking on the environment, but on the other hand natural gas as a fuel has fewer emissions than gasoline. For example, it releases less carbon dioxide, which is the greenhouse gas primarily responsible for global warming. Natural gas is mostly

methane, which itself is a potent greenhouse gas. So, to take advantage of the environmental benefits of natural gas, we must avoid additional emissions of methane as a result of this increase in the production, transportation, and use of natural gas.

If natural gas has economic and possibly environmental advantages over gasoline, why are most cars still running on gasoline? The problem is that natural gas suffers from a low energy density. The energy density is an important quantity, as it tells us how much energy we can obtain from a particular volume of fuel. The more energy we have in our fuel tank, the longer distance we can drive before we need to fill up our tank again. At room temperature and atmospheric pressure, one liter of gasoline, which is a liquid, has *950 times* the amount of energy of a one liter balloon of natural gas at the same conditions. The reason is that molecules are very far apart in a gas compared to in a liquid, leading to less molecules per volume. As a result, cars would need a fuel tank *950 times* the volume of current gasoline tanks to drive the same distance from a tank fill-up of natural gas at room temperature and atmospheric pressure. A typical gasoline tank can contain 50 liters; imagine what a car would look like with a tank 950 times bigger!

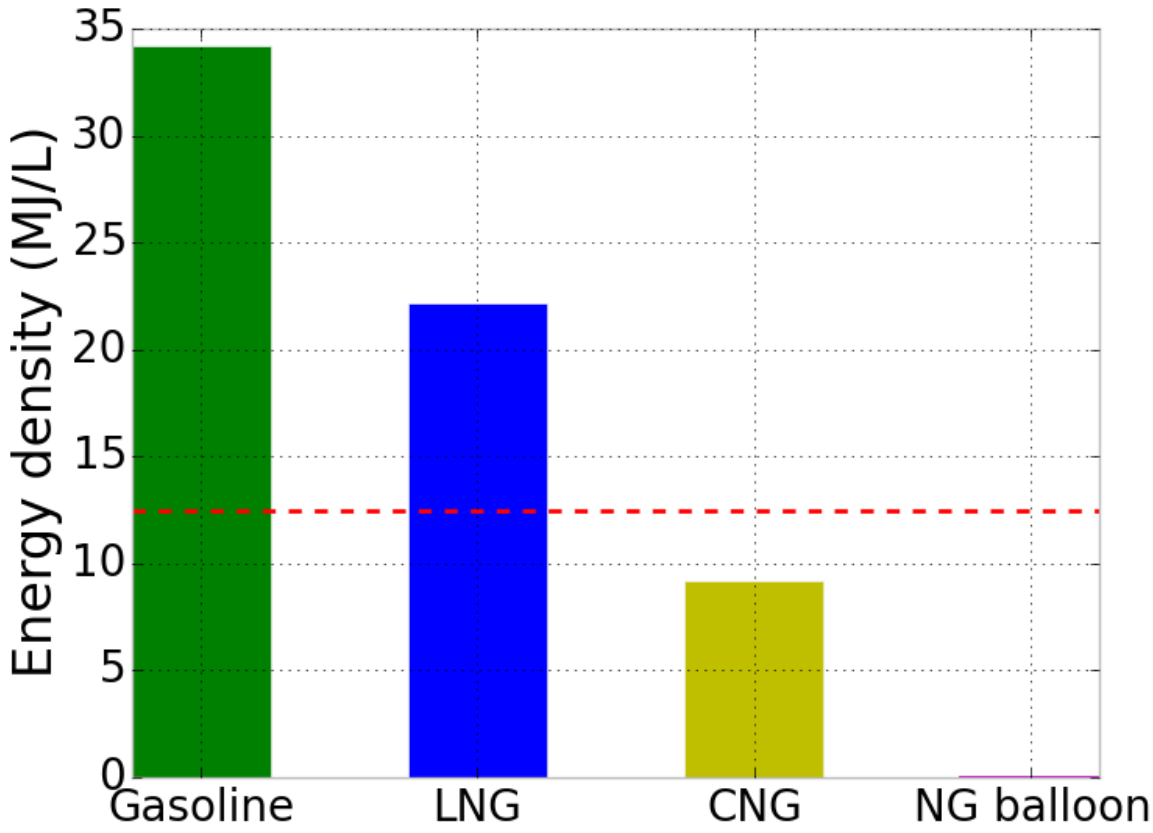

Figure 1: Energy density of fuels. We compare the energy densities of different fuels [1]. Gasoline has the highest energy density, almost 35 megajoules per liter (MJ/L). The next most dense fuel in terms of energy is

liquefied natural gas (LNG), and then compressed natural gas (CNG). On the far right, the energy density of a balloon of natural gas at room temperature and atmospheric pressure is so small (0.036 MJ/L) that we can barely see the magenta bar! The red, dashed line is the ARPA-E target energy density for storing methane in nanoporous materials; achieving this energy density of methane is the ideal outcome of research in adsorbed natural gas storage.

Thus, to utilize natural gas as a vehicular fuel without such impractically large fuel tanks, we need to put more methane molecules into the fuel tank. Two strategies are used today to increase the energy density of natural gas. One strategy is to compress natural gas; at a higher pressure, there are more gas molecules in the same volume. The other strategy is to cool natural gas to such a low temperature that it becomes a liquid, a process called liquefaction, since a liquid has a much higher density than a gas.

Increasing the density of natural gas

For liquefied natural gas (LNG), one cools the natural gas to a cryogenic temperature, around -162 °C, so that it condenses into a much denser liquid. LNG suffers from problems that prevent us from using it for passenger vehicles. The process to liquefy natural gas is energy-intensive. Bulky, expensive cryogenic fuel tanks are required to store LNG. Because the heat insulation on these tanks is not perfect, some LNG is vented into the atmosphere, instigating global warming and wasting fuel.

For compressed natural gas (CNG), one compresses the natural gas at room temperature to around 200 times atmospheric pressure. The problem with CNG is that the compression equipment to achieve such a high pressure is expensive. Furthermore, the onboard vehicular fuel tanks must have thick walls and a spherical or cylindrical shape to withstand such a high pressure and evenly distribute stress. This makes for a heavy, expensive tank, which only fits in the trunk of the vehicle, leaving no space for luggage. The tank that is used for gasoline, however, can be made of any shape and therefore is designed and placed to more efficiently use space in the car that is otherwise wasted.

In Figure 1, we compare the energy density of LNG and CNG to the energy density of gasoline. We also compare to a balloon of natural gas at room temperature and atmospheric pressure and see that LNG and CNG have a much higher energy density. While the density is not as high as gasoline, it is high enough that we can still drive quite a long distance with a CNG or LNG fuel tank.

Because of the difficulties with LNG and CNG, researchers are looking for alternative strategies to densify natural gas. One idea is to make a material that acts as a sponge for methane. [As natural gas is typically 95% methane, we will approximate natural gas as methane.] We then put this material inside the fuel tank and hope that it will adsorb so many methane molecules that we can achieve an energy density to compete with CNG, but now at a much lower pressure. Because the storage pressure is lower than in CNG, the fuel tanks can be thinner, cheaper, and made in any shape to more easily fit in the vehicle. In

addition, the compressors to achieve this lower pressure are cheaper than those for CNG, possibly enabling us to refill our tanks at home, using the same gas we are already using for cooking and heating.

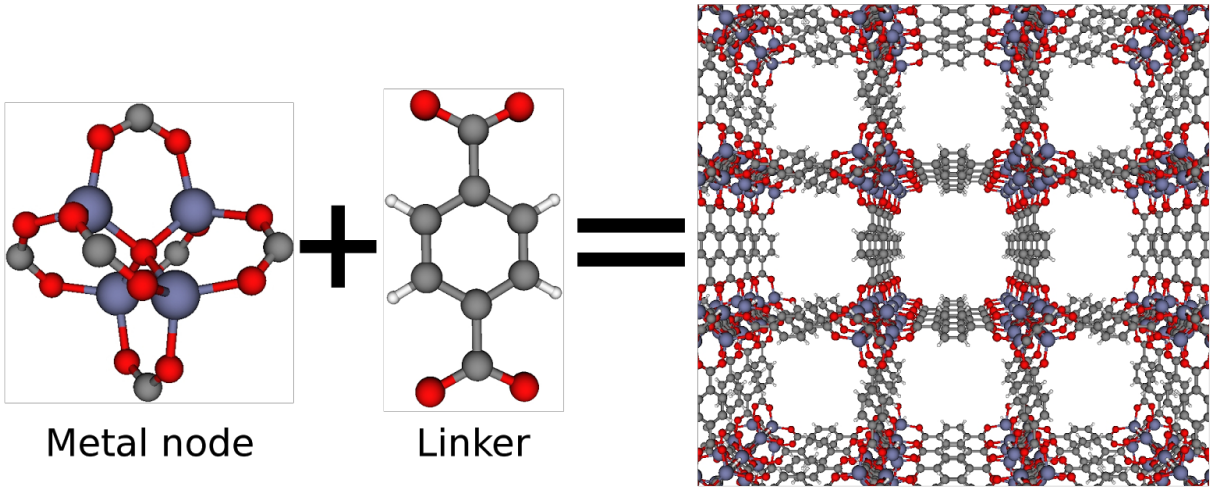

Figure 2: Example nanoporous material. On the right is the structure of a metal-organic framework (MOF) called IRMOF-1 [2]. IRMOF-1 is synthesized by combining two different molecular building blocks: metal nodes and organic linkers. These linkers and nodes self-assemble in solution to form the repeating nanoporous crystal structure of IRMOF-1. By changing the linkers and metal nodes, we can synthesize millions of different metal-organic frameworks. The spheres are atoms and the sticks represent chemical bonds. In the metal cluster that serves as a node, we see four blue spheres, representing zinc (the metal). The zinc forms into a cluster that serves as a node by connecting to oxygen atoms (red). The organic linker is a ring of carbon atoms (gray), on which hydrogen atoms (white) are connected. A carbon/oxygen group is present on two opposing ends of the linker, which will connect to the metal node during the assembly.

The materials that are the most promising sponges are *nanoporous materials*. A nanoporous material is a structure with nano-sized pores or cages. See Figure 2 for an example. A human hair is about 80,000 nanometers thick; a pore of a nanometer is so small that only *molecules* can fit inside. A methane molecule has a diameter of 0.3 nanometers, so each cage can store only a few methane molecules. A methane molecule interacts with and is attracted to the walls of the porous material. This attraction with the surface is a driving force that serves to recruit methane molecules into the cages of the material. To increase the energy density of methane, we need to attract many molecules. To get an idea of how many methane molecules a material can adsorb, we can look at the total area of the interior surface of these cages. A single gram of these nanoporous materials has the surface area of more than a football field; this provides a lot of attractive forces for adsorption.

The Advanced Research Projects Agency - Energy (ARPA-E) of the US Department of Energy initiated a multi-million dollar research program aimed to find a material for vehicular natural gas storage. In this program, ARPA-E set a research target that such a nanoporous material should achieve an energy density of 12.5 MJ/L (see red, dashed line in Figure 1). This target energy density corresponds to a density 340 times that of natural gas at room temperature and atmospheric pressure. The target was set to compete with CNG but using only ⅓ of the storage pressure of CNG. Researchers all over the world are trying to discover new materials that meet the ARPA-E methane storage target.

Finding the best nanoporous materials

An exciting aspect of advanced nanoporous materials is their chemical tunability. By combining different molecular building blocks, we can synthesize millions of different possible materials. For example, for metal-organic frameworks, an organic *linker* molecule combines with a metal *node* to form a repeating, 3D framework. See Figure 2. By changing the linker and node, we obtain millions of possibilities. The question is then how to choose the linker and node to tailor-make a material that is optimal for natural gas storage.

In a laboratory, it takes a few weeks to synthesize and test a new material. It would take too long to synthesize all these materials and test them for which adsorbs the most natural gas. This gives us important research questions: Out of the millions of possibilities, how can researchers know which combination of molecular building blocks will yield a material that meets the ARPA-E target storage capacity? How do we even know that the ARPA-E storage target is possible to reach? There are surely physical limits to how much natural gas a material can possibly store.

Making and testing materials on computers

Researchers have also been working on a method to make models of materials on a computer. By snapping together different molecular building blocks, much like they were Lego blocks, making materials on a computer goes much faster than in the laboratory. Once we have made a material on a computer, we can run computer simulations of methane adsorbing into the pores of the material. These computer simulations look like a flight simulator for molecules; we can predict how many methane molecules a given amount of material will adsorb on the basis of the computer-generated structures.

Researchers have constructed over 650,000 different nanoporous materials on computers to date by changing molecular building blocks and combining them according to rules based on what we know from the laboratory on how to synthesize these materials. We also have a dataset of over 4,000 metal-organic framework structures that have been synthesized in a laboratory already [3]. We then wrote an efficient computer code to simulate methane adsorption in these materials. Our computer code [4] runs on a specialized electronic circuit called a graphics processing unit (GPU), which was originally designed to handle computer

graphics but has recently been exploited in scientific computing. We then ran our computer code on these materials to predict the amount of methane that they will store.

From these calculations, we obtain a lot of data that we can learn from. Figure 3 gives an example. On the *y*-axis is the energy density of methane achieved in the material; on the *x*-axis is the crystal density of the material. The density of the material tells us the mass of the material (kg) per unit volume (m^3). Each dot in this graph is a material that was generated on the computer. We wanted to investigate how the energy density of methane depends on the crystal density. Let's think about this first. If a material has a very high crystal density, does this material have much space inside to store methane molecules? As we see in Figure 3, there is little room left for methane molecules to occupy; materials with a high crystal density achieve a low energy density of methane. Now let's think about the other case: a low crystal density. If the crystal density is zero, what do we have? Then we do not have any material at all, and we are back to a balloon, but at ⅓ of the pressure of CNG. As we see in Figure 3, methane energy densities achieved by materials with low crystal densities approach that of a balloon at ⅓ of the pressure of CNG, 2.5 MJ/L. In these structures, there are so little framework atoms per volume that there is not enough surface to provide attractions with methane molecules. The structures that achieve the highest methane energy densities have *intermediate* crystal densities, reflecting a tradeoff between making space for methane and providing material atoms for attractive interactions that recruit the methane molecules into the pores.

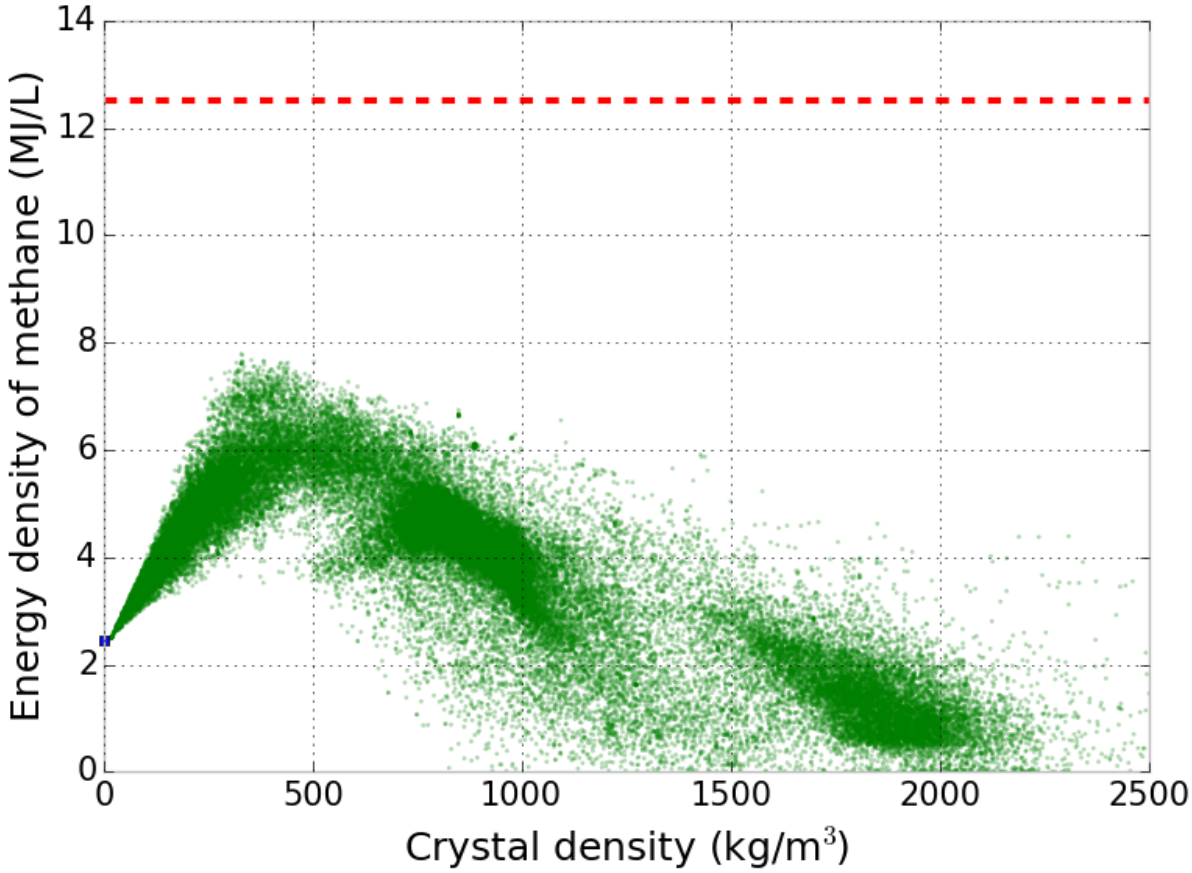

Figure 3: Molecular simulation results. Each point on this scatter plot is a nanoporous material structure. The y-axis shows the predicted achievable methane energy density (MJ/L) in the material, and the x-axis shows the crystal density (kg/m^3) of the structure. The blue square at (0 kg/m^3, 2.5 MJ/L) represents the performance of an empty tank-- without any material-- at the same conditions. The red, dashed line at 12.5 MJ/L is the ARPA-E storage target.

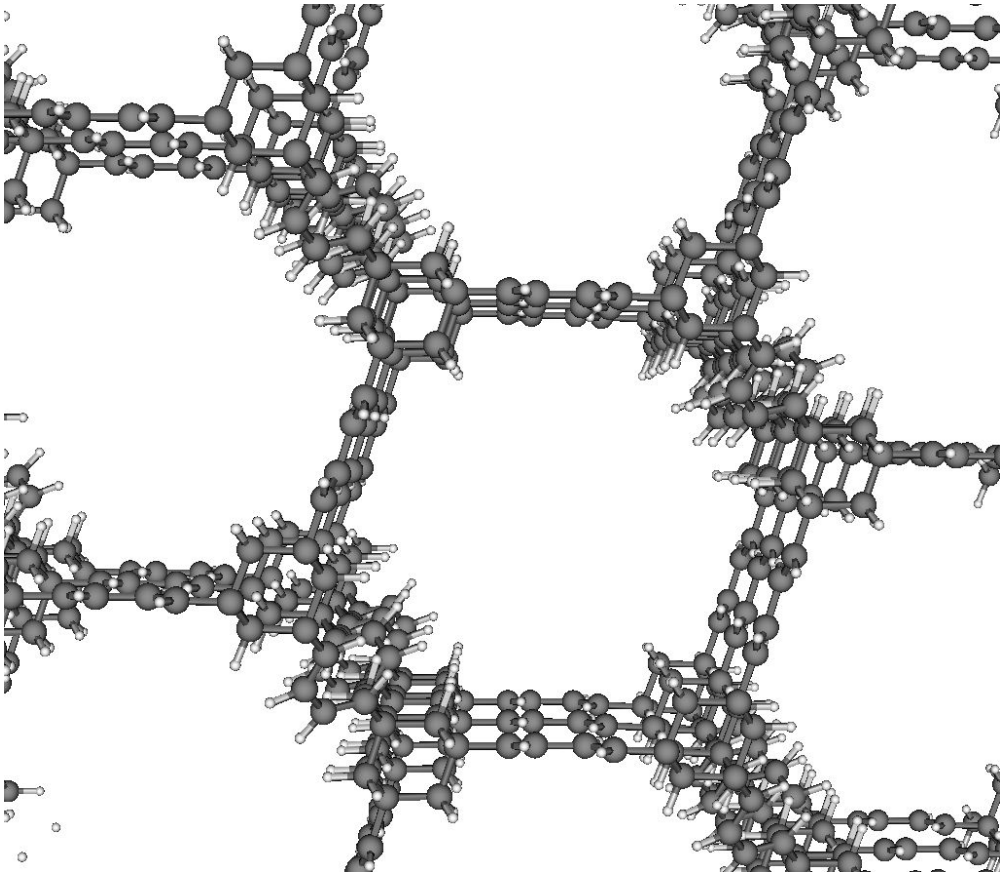

Figure 4: Top structure. The structure in our database that achieves the highest predicted energy density of methane-- 7.8 MJ/L-- is shown. The gray spheres are carbon atoms; the white spheres are hydrogen atoms.

The structure that we predicted to achieve the highest methane energy density is shown in Figure 4. This is a computer-generated structure [5] that has not yet been synthesized and tested for methane storage. The hope was to find among these 650,000 materials a few that would be above the red line in Figure 3, which is the ARPA-E storage target. However, the top material in Figure 4 achieved a predicted energy density of only 7.8 MJ/L-- only 62% of the ARPA-E storage target of 12.5 MJ/L. We then collected from the literature experimental measurements of methane adsorption in materials that have been synthesized and found that these too approach, at best, an energy density of ~8 MJ/L.

Our findings [6] suggest that there is not much room for improvement upon materials that have already been made and that the ARPA-E storage target likely cannot be reached. Recall that the storage target for materials was set to compete with CNG on economic grounds and not based on any physical arguments of limitations on methane storage capacities of materials. Our computational study of over half a million materials allowed us to access if the storage target is possible using physical arguments in a very short period of time. Still, a porous material that achieves an energy density of 8 MJ/L is a significant improvement over using an empty tank-- an empty tank at the same pressure achieves an energy density of 2.5

MJ/L. This improvement may be enough to drive the adoption of nanoporous materials for methane storage if we find a cheap and resilient material.

Conclusions

Can we now conclude that it is impossible to find a material that meets the ARPA-E target? First of all, it is important to realize that we only generate materials based on our current knowledge of how these materials are made in the laboratory. However, chemists could invent completely new classes of materials with superior performance. And, as we only looked at the presently known classes of materials, we cannot preclude such a miracle material. But our study shows that we do need a radically different approach or to assess whether the current materials are economically viable. One needs a slightly larger tank to get the same driving range as CNG, but this might be acceptable.

Nanoporous materials have applications in many other arenas, such as for separating gases, sensing chemicals, and controlling the delivery of drugs to the body. In each of these applications, one can use computer models and molecular simulations to identify the top candidate materials from our databases of materials, elucidate guidelines for synthesizing high performing materials, and identify limits to performance to set targets.

Acknowledgements

This article is the Young Minds version of a Perspective we have published in Energy and Environmental Science [6].

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