Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 November 2021 doi:10.20944/preprints202106.0212.v4

Sequestering biomass for natural, efficient, and low-cost direct air capture of carbon dioxide (Version 4)

Jeffrey A. Amelse [a,b,c] and Paul K. Behrens[d]

a) Universidade de Aveiro, Departamento de Química, CICECO, 3810-193 Aveiro, Portugal, JAmelse@UA.Pt
b) Independent Contributor and Chemical Industry Consultant, Batavia, IL USA, AmelseJeff@Gmail.com
c) Corresponding author
d) Independent Contributor and Chemical Industry Consultant, Greenfield, IN, USA PKBConsult2@Gmail.com

Keywords— Carbon Dioxide, Net Zero, Sequestration, Biomass, Direct Capture, Global Warming, Climate.

© 2021 by the author(s). Distributed under a Creative Commons CC BY license.

Abstract— Many corporations and governments aspire to become Net Zero Carbon Dioxide by 2030-2050. Achieving this goal requires understanding where energy is produced and consumed, the magnitude of CO_2 generation, and the Carbon Cycle. Many prior proposed solutions focus on reducing *future* CO_2 emissions from continued use of fossil fuels. Examination of these technologies exposes their limitations and shows that none offer a complete solution. For example, bioethanol is shown to be both carbon and energy inefficient. Direct Air Capture technologies are needed to reduce CO_2 *already* in the air. The most natural form of Direct Air Capture involves letting nature do the work of creating biomass via photosynthesis. However, it is necessary to break the Carbon Cycle by permanently sequestering that biomass carbon in “landfills” modified to discourage decomposition to CO_2 and methane. Tree leaves and biomass grown on-purpose, such as high yield switchgrass, are proposed as good biomass sources for this purpose. Left unsequestered, leaves decompose with a short Carbon Cycle time constant releasing CO_2 back to the atmosphere. While in any given year, leaves represent a small fraction of a tree’s above ground biomass, leaves can represent a substantial fraction of the total biomass generated by a tree when integrated over a tree’s lifetime. Understanding the chemistry of the distinct phases landfills undergo is the key to minimizing or eliminating decomposition. First, the compact cross-linked structure of cellulose and keeping water out will make it difficult for initial depolymerization to release sugars. Air ingress should be minimized to minimize Phase I aerobic decomposition. pH manipulation can discourage acid formation during Phase II. Lignocellulose is low in nutrients needed for anaerobic decomposition. Inhibitors can be added if needed. The goal is to move quickly to the dormant phase where decomposition stops. The cost for Carbon Capture and Storage (CCS) for growing and sequestering high yield switchgrass is estimated to be lower than CCS for steam reforming of methane hydrogen plants (SRM) and supercritical or combined cycle coal

power plants. Thus, sequestration of biomass is a natural, carbon efficient, and low-cost method of Direct Capture. Biomass sequestration can provide CO_2 removal on giga tonnes per year scale and can be implemented in the needed timeframe (2030-2050).

Introduction

Carbon dioxide is the dominant greenhouse gas leading to Global Warming. If man does nothing to intervene, atmospheric CO_2 levels are projected to more than double to over 900 ppmv by 2100 [1]. Many corporations and governments have set goals of Net Zero CO_2. A CO_2 material balance indicates: In – Out = Net Rate of Accumulation. To achieve Net Zero CO_2, CO_2 removal must equal CO_2 generation, which was 36 giga tonnes/yr (Gt/yr) in 2016. Preferably CO_2 removal from the atmosphere exceeds generation to reduce the level of CO_2 *already* in the atmosphere, which is already leading to Global Warming. Many new technologies for confronting CO_2 accumulation and fuels decarbonization are under rapid development. These include technologies for renewable energy, biofuels, hydrogen production from fossil fuels with Carbon Capture and Storage (CCS), and CO_2 removal and sequestration from large point source industrial furnaces. Most focus on reducing *future* CO_2 emissions from continued use of fossil fuels. This manuscript serves as both a wake-up call that prior proposed technologies fall far short of what is needed to achieve Net Zero, and a proposal for a simple natural low-cost method that can reduce net CO_2 emissions on a Gt/yr level. In the proposed method, biomass is grown from atmospheric CO_2 via photosynthesis and then removed from the Carbon Cycle by permanent burial in landfills modified to discourage decomposition.

Methods for removing CO_2 *already* in the air are known as Direct Capture methods. In one direct air capture technology, being developed by companies such as Climeworks and Carbon Engineering, large fans blow air through an adsorbent or absorbent [2,3]. The CO_2 must then be released by adding heat, followed by CO_2 compression and cooling to liquify to allow it to be transported for industrial uses or permanent storage underground. There are numerous issues with this technology that put current estimates of the cost of recovered CO_2 as high as $800/tonne [4]. An enormous amount of air with 400 ppm CO_2 must be moved through the adsorbent to remove even a small amount of CO_2. The fans have high capital and operating cost.

One issue for decarbonization by CO_2 recovery is what to do with the recovered CO_2. CO_2 has value for certain markets, such as carbonation of beverages and tertiary oil recovery. However, the markets where CO_2 have value are small compared to the current 36 giga tonnes/yr (Gt/yr) generated. Beyond those markets, recovered CO_2 has negative value, and CO_2 must be stored underground in spent oil or gas wells or in saline aquifers.

A 2005 US Energy Information Authority (EIA) report estimated that the markets where CO_2 has value extend to about 700 million metric tonnes per year (Mt/yr), well below the 36 Gt/yr total generation [5]. EIA identified geological formations having a total storage capacity of about 3800 Gt CO_2, which is enough storage capacity to remove CO_2 generation for many years to come. However, underground storage comes at a cost. The mean cost for storage in deep saline aquifers was estimated to be about $12.5/t CO_2 in 2005, which is $17/t CO_2 in 2020 when escalated using the US Consumer Price Index (CPI) [5].

There is a lot of focus on the use of hydrocarbons such as methane to produce hydrogen as a clean burning CO_2-free fuel. However, methane is 12/16 mass units carbon, and the carbon must go somewhere. In the steam reforming of methane (SRM) to produce hydrogen, the carbon ends up as CO_2 that must be recovered and permanently sequestered.

Hydrogen can be produced by SRM or partial oxidation of other hydrocarbons. For natural gas, the preferred route is SRM. In a first step, methane is reacted with steam at high temperature to form a synthesis gas ($CO + H_2$):

$CH_4 + H_2O = CO + 3\ H_2$ 1)

This reaction is strongly endothermic: ΔHr = 206 kJ/mol

In a second step, the CO is reacted with more water via the water-gas shift reaction to form more hydrogen plus CO_2:

$CO + H_2O = H_2 + CO_2$ 2)

This reaction is mildly exothermic: ΔHr = -41 kJ/mol.

The net reaction is:

$CH_4 + 2\ H_2O = 4\ H_2 + CO_2$ 3)

The net reaction remains strongly endothermic: ΔHr = 165 kJ/mol.

Thus, a large amount of heat must be put into the process. That heat generally goes into the reformer process furnace by burning additional natural gas. Of course, the furnace flue gas contains CO_2. For hydrogen from steam reforming to be a "CO_2-free" fuel, both the CO_2 produced by the reactions and CO_2 in the furnace flue gas must be recovered and sequestered. Recovery of CO_2 from SRM will be examined in more detail below.

For low molecular weight hydrocarbons with low C:H ratio, steam reforming is preferred. For hydrocarbons with high C:H ratios, such as coal, or even elemental carbon, partial oxidation is preferred, as shown in Equation 4 for pure carbon:

$C + ½\ O_2 \rightarrow CO$ 4)

Theoretically, any hydrocarbon can be steam reformed or undergo partial oxidation and the CO reacted with water to produce hydrogen and CO_2 via Reaction 2.

An understanding of the Carbon Cycle indicates that the only practical way to remove CO_2 *already* in the atmosphere is to grow biomass from atmospheric CO_2 and then permanently remove that biomass carbon from the Carbon Cycle. Steam reforming or partial oxidation of biomass, followed by water-gas shift and CO_2 capture and storage is one way. However, it is expensive, since it requires high capital, energy and other operating and fixed costs for CCS. The need for process energy reduces the effective net CO_2 removal. If process fuel is fossil fuel, even more biomass is needed to compensate for the CO_2 generated by this fuel. Even if the fuel is biofuel, the carbon burned in the fuel reduces the yield of biomass carbon that actually contributes to CO_2 removal. The cost of CCS for an SRM hydrogen plant will be calculated and compared to CCS for growing biomass and sequestering the biomass carbon.

Growing biomass from atmospheric CO_2 via photosynthesis and biomass sequestration is the simplest most natural way of Direct Carbon capture. This is *Carbon Sequestration* as opposed to *CO_2 Sequestration*.

Tree leaves are proposed as one good source of biomass for sequestration. Leaves are shown to represent a significant portion of the total biomass generated by a tree when integrated over the life of a tree. Left unsequestered, leaves decompose and release their carbon as CO_2 back to the atmosphere to complete their Carbon Cycle. Sequestering leaves as opposed to tree trunks and branches would have the advantage of leaving the underlying forests undisturbed. Furthermore, trees have a very long Carbon Cycle time constant on the order of decades to centuries, as opposed to leaves which have a short decomposition time constant on the order of a year and are renewed every year.

Of course, other sources of biomass should be considered, such as municipal waste, or crops grown on-purpose for sequestration. High yield switchgrass would be a particularly good source of biomass. In fact, growing and sequestering switchgrass for the purpose of direct CO_2 capture may have certain advantages over gathering leaves. Growing switchgrass is very analogous to growing hay which is well established farm technology practiced on a massive scale. The cost of harvesting hay is well known [6]. The cost of harvesting switchgrass should be very similar. Together, sequestering tree leaves and switchgrass has the ability for Direct Air Capture of Gt/yr CO_2.

1. The energy scene

Before discussing the proposal, it is helpful to examine the current energy scene, i.e., what fuels are used, where they are used, and to examine the current world energy consumption by fuel source, and the amount of CO_2 currently being generated each year to understand the magnitude of the problem and show that prior proposed technologies fall far short of the goal of achieving Net Zero CO_2 by 2050.

The US Energy Information Authority (EIA) provides a database that tracks primary energy production and disposition for the US, and other world regions [7]. BP provides its yearly Statistical Energy Review [8].

Fig. 1 shows the US 2016 (pre-pandemic) primary energy source and sector in which the energy is used [9]. The three largest sources are petroleum (37%), natural gas (29%), and coal (15%). In 2016 only about 10% of primary energy came from renewables.

The numbers on the left of the lines connecting sources to usage sectors show the percentage of a source that goes to a corresponding sector. The major sectors are transportation (29%), industry (22%), and electric power (39%). Industrial use accounts for 22% and residential and commercial accounts for 11%.

The numbers on the right of **Fig. 1** show the percentage of energy used in a sector that comes from the corresponding source. Thus, 71% of petroleum goes to the transportation sector with most of the balance (23%) going to industry, and only minor amounts to residential and commercial and electric power sectors. Natural gas usage is split almost evenly amongst industrial, residential and commercial, and electric power, with very little to transportation. Coal and nuclear are almost exclusively used to generate power.

In 2016, CO_2 emissions were 36 Gt [9]. The world has a huge CO_2 problem that is going to take a variety of huge solutions to solve. **Fig. 1** shows the US energy demand. World energy demand is different. In particular, coal represents a much higher fraction of energy demand in China. China dominates world energy demand. Asia and Oceania account for almost half of total energy demand., Thus, it is not surprising that coal and coke (a heavy-end solid refinery byproduct that can be substituted for coal) represent about 44% of total energy demand. Petroleum and other liquids represent about 36%, and natural gas about 20%. Coal usage in China exceeds that in the rest of the world combined, as shown in **Fig. 2**. Thus, while coal usage is declining worldwide, it will continue to play a major role in China, and a solution is needed for the CO_2 coming from coal.

The EIA provides a projection for the shift in all energy sources for electricity production (**Fig. 3**), and further granularity for the sources of renewable energy for electricity production out to 2050 (**Fig. 4**) [10]. Coal is expected to decline from 24% to 13%, and nuclear is expected to decline from 19% to 12%. Renewable energy is projected to double but will still be under 40% of the total energy sources.

The absolute amount of electricity from wind is projected to double. Solar is projected to increase by a factor of 9. Is that a reasonable projection? Natural gas has become cheap and abundant in the US after the advent of fracking. The EIA projects that the fraction of electricity coming from natural gas remains about constant near 36 to 37% out to 2050. This is still a very significant percentage and a significant percentage of CO_2 production. Thus, a means to sequester CO_2 during the production of electricity from natural gas is needed, especially if the projected increase of electricity from solar falls short.

The energy for transportation is distributed between passenger cars, long haul trucks, aviation, rail, and marine. US passenger cars are currently fueled primarily by gasoline. Thus, in the US, gasoline represents about 47% of refined products [11]. Distillates represent about 30%, with LPG (7%) and Other Petroleum Liquids (chemical feedstocks, etc.) representing the balance. US distillate fuels represent about 20% of US refined products with about 67% of distillates used for on-highway diesel mainly for long haul trucks. Thus, the gasoline:distillate ratio in the US is: 47:30 = 61%:29%. Jet fuel is about 8% of US refined products [12]. Diesel cars are more popular in Europe. Thus, for example in Germany, distillate fuel oils represent about 46% and gasoline only about 18% of refined products [11].

US gasoline currently contains about 10 vol% bioethanol. Thus, bioethanol represents only a very small amount of total US energy consumption:

(29% transportation of total x 61% gasoline x 10% ethanol = 1.8%), and that comes at great economic and social cost. Currently about 40% of the US corn crop is devoted to fuel ethanol [13]. Furthermore, the stoichiometry of the fermentation reaction converts only 4 of the 6 carbons in glucose sugar formed by hydrolysis of corn starch to ethanol and 2 carbons to CO_2:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 \qquad 5)$$

The vent gas from bioethanol plants in nearly pure CO_2. Thus, it does not require equipment for separation, and it is the easiest large industrial CO_2 stream to capture and sequester. However, currently most US ethanol plants vent the CO_2 to atmosphere. The 4 out of 6 sugar carbons that go to bioethanol represent renewable carbon that will displace *future* fossil fuels from continued gasoline production. They will not reduce CO_2 *already* in the atmosphere. Only the 2 of 6 carbons that go to CO_2 during fermentation will represent Direct Capture CO_2, and only if bioethanol plants are fitted with CCS.

The overall carbon efficiency of converting a corn plant into either corn ethanol or CO_2 from ethanol fermentation that could contribute to pulling CO_2 from the air with ethanol plant CCS is quite small. A corn plant is about 30 wt% corn kernels. Corn kernels are about 70% starch which is hydrolyzed to glucose sugar. Only 4 of 6 carbons in the glucose go to ethanol, and 2 go to CO_2. Thus, the carbon efficiency is about:

(30% kernels x 70% starch x 4/6 carbons to ethanol) = 14.0% for ethanol

(30% kernels x 70% starch x 2/6 carbons to CO_2) = 7.0% for CO_2

This will be one of the main advantages for biomass sequestration. Secure sequestration of biomass has the potential to achieve near 100% of the biomass carbon from the Carbon Cycle if decomposition can be prevented.

Bioethanol is not break-even sustainable, when the energy used to produce the corn and used within the process is considered. Water removal from the ethanol fermentation mixture is very energy intensive. The energy needed just to remove water to the azeotropic composition is about 18% of the heat of combustion of the ethanol product [14]. The total energy for a Dry grind ethanol plant can be as high as 33% of the heat of the product combustion [15].

There are a few new projects to capture and store CO_2 from bioethanol plants. ADM has one in operation in Illinois [16]. That project cost \$208 MM, with 68% paid by the DOE, and was designed to capture about 1 million short tons CO_2 per year. The captured CO_2 is stored underground in a saline aquifer nearby, so minimal pipe distance was required. With actual plant operating factor of about 80%, it is capturing about 728 metric tonnes per year (Mt/yr). The simplest way to express a capital charge is as an annuity at x percent interest rate for y years. In this document, this will be referred to as a “x% PI, y year capital charge.” Note this is independent of taxes and any government incentives, and thus is a good representation of the true cost. Project life and interest rate are variables set by investors in projects. The cost of capital for a corporation can be calculated from corporate balance sheets. A corporation’s acceptable project return rate for them to invest in a project is generally greater than their cost of capital. For the ADM project, with a conservative interest rate, the 6% PI, 20 yr year capital charge is \$24.5/metric tonne CO_2. A 10% PI, 15 yr capital charge would be \$36.9 / metric tonne.

Other announced projects for CO_2 capture from bioethanol plants include the Summit Agricultural Group and Green Plains, Inc. project to capture CO_2 from several bioethanol plants in Iowa and Minnesota [17], North and South Dakota with CO_2 storage in a saline aquifer in North Dakota, and a planned 1200 mile CO_2 pipeline (not yet a CO_2 capture and storage project) by Valero and Blackrock that will span the Midwest designed to send up to 5 Mt/yr CO_2 to storage in a saline aquifer in southern Illinois [18]. Note that these projects are very small (Mt/yr) compared to the Gt/yr CO_2 being generated, which reemphasizes the need for other solutions.

Bioethanol from cellulosic biomass has been a long-term goal due to potentially cheap feedstock and no diversion of food to fuel. A 2009 Sandia study indicated that 70 billion gallons of cellulosic ethanol should be “possible” by 2030 [19]. However, almost 10 years later, only about 15 million gal were produced in 2018 [20]. The reality is that continued economic and technical challenges remain. Unlike the sugars polymerized to form mainly linear chains in corn starch, the sugars in lignocellulose cross link and densely pack, making cellulose insoluble in water, and thus, the first step, attack of the linkages via hydrolysis is very difficult. Pretreatment to release the sugars requires high temperature treatment by corrosive acids or bases or expensive enzymes, such that the cellulose pretreatment step can be one third of the total capital for cellulosic ethanol.

Biodiesel penetration into the total diesel market is even lower than bioethanol penetration at about 6% of diesel for on-highway use (only about 4% of total US distillate oils), and that consumes about 30% of US soybean oil [21,22]. It also consumes corn oil in a ratio of about 27 liters corn oil to about 73 liters soybean oil [21,22]. Corn oil is the most valuable product from corn wet mill plants, and thus is an expensive feedstock. One problem for biodiesel is that the reaction of vegetable oils to produce fatty acid methyl esters (FAME), which are the components of biodiesel, produces 10 units of glycerin for every 100 units of FAME. Glycerin is a nuisance byproduct that must find a home to improve biodiesel economics.

The future for zero CO_2 emission passenger cars is electric vehicles. Powering them by renewable electricity would make them net zero CO_2 emitters (not counting CO_2 related to their manufacture and battery production). The reality is that electric vehicles represented only 1.5% of new vehicle sales in Q1 2019 [23]. Also, recall that EIA projections are that natural gas will still account for 36% of electricity generation in 2050 needed to power them (**Fig. 3**), and electric passenger cars represent only a portion of energy for transportation, which accounts for only about 30% of total energy consumption. Long haul trucks, rail and aviation represent a significant fraction of transportation energy. Currently there are no practical electric drives for those modes because the number of batteries required are too large.

Clearly, other solutions are needed to achieve net CO_2 emission goals by 2050.

2. Understanding the Carbon Cycle

The Carbon Cycle is misunderstood by many. There are those who believe planting more trees will lead to a reduction in atmospheric CO_2. It is true that deforestation and burning of forests to clear land leads to a *temporary* large release of CO_2, and reforestation leads to *temporary* reduction of atmospheric CO_2. However, when trees are followed through their entire life cycle, trees are sustainable. They pull CO_2 from the air for growth during their life. However, in unmanaged forests, tree biomass eventually decomposes, and a tree's stored carbon is released back to the atmosphere as CO_2. Thus, trees are sustainable. Over their entire life and death cycle, planting trees in unmanaged forests will not lead to a net reduction in CO_2 that is *already* in the atmosphere.

Trees lose their leaves every year, which decompose and release their stored carbon back to the atmosphere on a time scale of approximately one year. In any given year, leaves represent a small fraction of the above ground tree biomass. However, it will be shown that when integrated over the life of a tree, they can represent a substantial biomass generated during the life of a tree.

Plants get all of their carbon for their growth from CO_2 in the atmosphere via photosynthesis, forming mainly carbohydrates [24]. The photosynthesis reaction can be represented crudely by the reaction:

$$6\ CO_2 + 6\ H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6\ O_2 \qquad 6)$$

The simplest formula representation of carbohydrates is CH_2O, Thus the amount of CO_2 plants pull from the atmosphere can be calculated roughly from plant mass using the ratio of molecular weights: (44.01 gm/mol CO_2)/30.03 gm CH_2O). Lignin in plants is a complex polymer of alkylaromatics (no oxygen), which does throw off this ratio a bit, so this is an approximation.

Plant matter is fed to animals and plants and animals are fed to humans. Animals and humans respire the bulk of the carbon in their food as CO_2 when they exhale. Animals and humans grow and thus serve as temporary storage vessels for some of the carbon. However, plants, animals, and humans eventually die and decompose and release their carbon back to the atmosphere as CO_2, completing their part of the Carbon Cycle. Plant matter left on the ground decomposes via the action of worms, fungi, and bacteria. They feed on the decomposing biomass, and respire CO_2, and thus, play an important role in the Carbon

Cycle. Normally there is no net buildup of carbon in the soil. Soil carbon generally reaches a steady state carbon level of 1-4 weight percent (wt%) [25]. Depending on farming practices, there can be a small increase or decrease of plant matter carbon in the soil. However, it is small and limited. If there were a large net movement of carbon to the soil, mountains would spring up in the US corn belt, and that is clearly not the case.

While plants receive all of their carbon from the atmosphere, they draw water as a source of hydrogen, nitrogen, phosphorous and other nutrients such as potassium from the soil. The enzyme that catalyzes photosynthesis contains both nitrogen and phosphorous [24]. In the natural Carbon Cycle, dead plant material returned to the soil feeds the worms, bacteria, and fungi that decompose it releasing the needed N, P, K, and other nutrients back into the soil. That is part of the Carbon Cycle. Intensive farming requires artificial fertilizer to provide some of the nutrients removed with the farm products.

Thus, the normal Carbon Cycle is sustainable. Over time, there is no net movement of CO_2 to the atmosphere and no net movement of carbon into the soil. The only way to remove CO_2 *already* in the atmosphere is to break the cycle. Biomass must be grown from CO_2 in the atmosphere and the biomass itself must be sequestered (*Carbon sequestration, not CO_2 sequestration*).

3. **Sequestration of biomass *carbon***

As noted earlier, renewable energy, biofuels without CCS, and CO_2 sequestration will reduce *future* CO_2 from continued use of fossil fuels entering the atmosphere. However, doing it on a scale needed to meet current and future energy demands is daunting. Furthermore, these are not a complete solution to achieve Net Zero CO_2, so other solutions are needed.

Per an understanding of the Carbon Cycle, the only practical way to remove CO_2 *already* in the atmosphere is to grow biomass and remove that biomass from the Carbon Cycle by permanent sequestration.

If the biomass in the entire corn plant from the 40% of the US corn crop that is now devoted to bioethanol production were sequestered and removed from the Carbon Cycle, instead of just the starch in the corn kernels going to bioethanol, that would be the equivalent of removing 407 Mt/yr of CO_2 per year compared to the 36 Gt/yr CO_2 generated. Something else is needed to achieve Net Zero CO_2.

In this manuscript, secure burial of biomass from other sources, including municipal and yard waste and biomass generated in forests (tree leaves and wood) or from growing high yield crops, such as switchgrass is proposed as a supplemental solution. Secure burial means permanent burial with provisions taken to prevent decomposition and release of the CO_2 to the atmosphere. Thoughts on how to achieve secure sequestration with minimal or no CO_2 to the atmosphere are provided in the next sections.

Permanent sequestration of municipal and yard waste in permanent landfills would remove that carbon from the Carbon Cycle and would remove CO_2 *already* in the atmosphere that would feed the growth of the organic materials in those waste sources.

Most municipal yard waste is buried in landfills. Some municipal waste is now burned to generate renewable power. One issue for that application is that even after separation of recyclables, average municipal waste still contains about 20% non-organics (glass, metal, etc.), as shown in **Fig. 5** that must be separated before the organics can be burned [26]. Secure landfilling to sequester all of the waste would not require this stringent and costly separation.

How big of a difference could secure sequestration of municipal and yard waste make? The US EPA provides statistics on municipal and yard waste generated, and how much is ultimately landfilled [26]. In 2017, the total amount of US municipal and yard waste generated was 243 Mt. Some is separated and recycled, and some is currently burned to generate renewable power, leaving the amount landfilled at 127 Mt, with composition provided in **Fig. 5**. The organic component was 102 Mt. That corresponds to about 150 Mt of CO_2 if allowed to completely decompose. This compares to the 5.9 Gt per year CO_2 generated in the US and is far short of the 36 Gt/yr CO_2 currently being generated worldwide. Participation by other countries would help, but clearly not enough to solve the daunting CO_2 problem.

Other biomass is needed for pulling CO_2 from the atmosphere: trees, both tree leaves and/or wood, and high yield crops. The USDA has provided allometric equations for urban tree growth parameters for many species and at numerous locations in the US [27]. The growth equations have been programmed into EXCEL files which are available in the Supplemental Input **SI.1**. Dry leaf biomass is calculated for most species and regions where data are available.

Dry leaf biomass for some species of maple trees at various locations in the US are shown in in **Fig. 6**, as an example. Data for other tree species are provided in **SI.1**. Dry leaf biomass can be over 100 kg/yr for some of the maples and over 400 kg/yr for some of the oaks depending on location and age.

Leaves currently fall to the ground and decompose every year. Assuming a conservative average of 50 kg/yr dry weight of leaves per tree, if forests were managed, the leaves gathered and permanently securely buried, this would be the equivalent of over (50 kg/yr dry mass)*(44.01 gm CO_2/30.03 gm CH_2O) = 73 kg/yr CO_2 removed from the atmosphere per tree every year.

According to the latest estimate, there are over 3 trillion trees in the world [28-29]. However, only about 30% of the trees are deciduous. At 73 kg/yr-tree CO_2 equivalent per tree that is the potential to remove 66 Gt/yr CO_2, compared to 36 Gt/yr CO_2 generated each year. Thus, theoretically sequestering tree leaves could provide a complete solution to our CO_2 fossil fuel problem. The potential is enormous but sequestering all of those leaves would be daunting.

One secondary issue for sequestering biomass will be the replacement of P, N, and K nutrients needed for photosynthesis. This can be done via chemical fertilization. Fertilizer production will generate CO_2, but this can be compensated by additional biomass sequestration.

Mature tree wood weights can be several metric tonnes per tree, as shown in **Fig. 7**. Removal and secure burial of tree wood would help. However, there are several issues. First, tree trunks and tree branches have a much longer Carbon Cycle time constant (on the order of decades or centuries) compared to leaves (on the order of one year). However, it is not needed. Harvesting leaves would suffice. While the mass of leaves dropped in a particular year is much less than that of the tree trunk and branches, leaf mass becomes appreciable relative to the latter when integrated over the life of the tree. Also, harvesting leaves alone would not disrupt the forest itself, and leaves are renewed every year. It is best to leave the wood for its current uses (construction, furniture, etc.). Managing new forest plantings should be considered with access provided for leaf collection. In Brazil, secure burial of excess bagasse beyond that needed for plant power generation should be considered. The bagasse is already at the ethanol plant. It could be buried in a site nearby to minimize transportation costs. Sequestration of other biomass, such as underbrush should also be considered.

Figs. 6 and **7** represent calculations from the regression equations for the allometric tree growth equations provided by McPherson, van Doorn, and Peper (2016) [27]. Twelve equation forms were used for different species and different locations, including quadratic, cubic, quartic, exponential and ln(ln). Some are not well behaved for extrapolation. Thus, they were not extrapolated beyond the limits provided. However, even within the limits, some projections showed declines in mass with age, and thus, were truncated at the point where that happened.

Fig. 8 provides calculated cumulative leaf biomass as a percentage of total tree biomass generated (including tree trunk and branches) up to a given tree age. Note that the calculations show some erratic behavior from the combining of two ill-behaved correlations in some cases. Considerable scatter is observed depending on species and location. Nonetheless, this figure shows that the cumulative leaf mass can be a significant fraction of the total tree biomass generated over the life of the tree. In certain cases, the regressed percentage of leaf biomass exceeds 50% to over 70% of the total biomass generated over the life of the tree.

4. Modified landfills for biomass *carbon* sequestration

Permanent sequestration of municipal waste and plant biomass will require rethinking how landfills are designed. Currently, landfills are designed to allow or even encourage some decomposition of the waste

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 November 2021 doi:10.20944/preprints202106.0212.v4

to minimize volume, such as in the current trend towards municipal waste bioreactor landfills. Permanent sequestration requires discouraging waste degradation in landfills.

Municipal waste is buried in landfills, where a portion slowly decomposes. It undergoes a combination of aerobic and anaerobic decomposition to produce a biogas. Modern municipal waste landfills undergo several distinct stages [30-32]. Understanding the chemistry of the phases provides clues on how to disrupt decomposition at each phase.

Phase I (Initial Adjustment)

During the first phase of decomposition, aerobic bacteria that require oxygen to live consume oxygen while breaking down the complex carbohydrates, proteins, and lipids that comprise organic waste. The primary byproduct of this process is carbon dioxide. Nitrogen content is high at the beginning of this phase, due to nitrogen in the air that supplies the oxygen for aerobic decomposition. Nitrogen content continuously declines as the landfill moves through the phases. Phase I continues until available oxygen is depleted. Phase I decomposition can last for days or months, depending on how much oxygen is present when the waste is disposed in the landfill, which can vary depending on how compacted the waste was when it was buried. Starving the biomass of oxygen by minimizing air infiltration during Phase I may discourage anaerobic decomposition during Phase I.

Phase II (Acid Phase)

Phase II decomposition starts after the oxygen in the landfill has been depleted. Anaerobic bacteria then convert compounds created by aerobic bacteria into acetic, lactic, and formic acids and alcohols such as methanol and ethanol. The landfill becomes highly acidic. With the presence of moisture, the acids cause certain nutrients to dissolve, making nitrogen and phosphorus nutrients available to the bacteria present during this phase. The biogas comprises mainly carbon dioxide and hydrogen during this phase. pH adjustment by adding bases might be used to disrupt nutrient release during Phase II.

Phase III (Methane Formation)

Phase III decomposition starts when anaerobic bacteria consume the organic acids produced in Phase II and form acetates. This process causes the landfill to become a more neutral environment in which methane-producing bacteria establish themselves. Methane- and acid-producing bacteria have a mutually beneficial relationship. Acid producing bacteria create compounds for the methanogenic bacteria to consume. Methanogenic bacteria consume the carbon dioxide and acetate, too much of which would be toxic to the acid-producing bacteria.

Phase IV (Stable Phase)

Phase IV decomposition begins when both the composition and production rates of landfill gas remain relatively constant. Phase IV landfill gas usually contains approximately 45% to 60% methane by volume, and 40% to 60% carbon dioxide.

Phase V (Mature Phase)

Landfills eventually enter a mature phase. The rate of microbiological activity slows during this phase as the supply of nutrients and/or moisture limits the chemical reactions. CH_4 production almost ceases completely. Thus, the fraction of biogass that decomposes reaches an asymptote.

The anaerobic decomposition phase produces a biogas. On average, about half of the volumetric concentration of landfill gas is methane and slightly less than half is CO_2. Methane has a climate change potential that is 25 times more powerful than CO_2. Thus, anaerobic decomposition is to be discouraged in the landfills proposed for biomass sequestration.

Landfills are now designed with underground collection systems, and the gas is typically routed to flares, and burned as a renewable fuel. Thus, the carbon in the gas is converted to CO_2 which goes back to the atmosphere. Some landfills now route the gas to boilers for power generation (renewable power generation), or other uses. The high CO_2 content of biogas makes it ripe for CO_2 recovery and sequestration. CO_2 sequestered from biogas would represent true Direct Capture from the air used to generate that biomass.

How can landfills be redesigned to minimize or eliminate biomass degradation? By understanding the degradation chemistry, there are opportunities to interrupt the process at each phase. Phase I degradation could be minimized by minimizing the landfill working volume as material is moved to the non-working volume which is moving towards later phases. The working volume may be covered by tarps at night or covered by foam. This is already being done in some landfills. Nitrogen blanketing could eliminate the oxygen needed for aerobic decomposition. The nitrogen could come by recycling the high nitrogen content of the oxygen depleted air that represents early biogas generated during Phase I.

Simplified equations for anaerobic degradation of cellulose are:

$$(C_6H_{10}O_5)_n + n\ H_2O \rightarrow n\ C_6H_{12}O_6 \qquad 9)$$

Reaction 9 represents hydrolysis (depolymerization) of cellulose to release sugars.

$$n\ C_6H_{12}O_6 \rightarrow 3n\ CH_4 + 3n\ CO_2 \qquad 10)$$

Reaction 10 represents anaerobic digestion to form methane and CO_2.

Water is needed to first depolymerize the starch or cellulose to release the sugars that serve as food for the anaerobic bacteria. Thus, one key to reducing or eliminating anaerobic degradation is to keep water out, i.e., preferably to dry the biomass in drying fields, and sealing the landfill as it moves beyond Phase I.

Another way to discourage anaerobic decomposition is to exploit known inhibitors of anaerobic bacteria [33]. These include among others, pH adjustment, high concentration of alkali or alkaline earth metals, etc.

Municipal waste used to be accumulated in open piles. Modern landfills with daily, intermediate, and final covers only began in the 1940s and accelerated in the 1960s and 1970s. None of the modern landfills have gone through their full life cycle, which can take hundreds to thousands or even millions of years. The evidence is the huge mounds that are left by modern landfills that have had their final earthen caps installed and are then abandoned.

Can secure permanent sequestration of biomass carbon really be achieved? The answer is: Yes, it can. Can some leakage be tolerated during the five stages? The answer is: Yes. However, it will increase the amount of material that needs to be sequestered to compensate for these losses. Some biogas can be allowed and collected and burned to generate renewable power to displace fossil fuels as is currently done at many landfill sites.

Thus, secure permanent landfills are envisioned that are modifications of current landfills. These landfills may also be located near the source of biomass to minimize transportation cost.

5. Modelling biomass degradation in a normal landfill

Steps to reduce or eliminate biomass degradation are desirable but will add cost. Are they absolutely necessary? To answer this question, the degradation of switchgrass in a normal landfill was modelled.

Coscuner, et al. [34] modeled landfill gas generation in a landfill in Bahrain. using the US Environmental Protection Agency's Landfill Gas Emission Model software [35]. The data in Tables 1 and 2 of that manuscript allow the calculation of the fraction of the fraction of decomposable waste that is predicted to decompose following landfill closure. That landfill opened in 1987 and closed in 2019. The total amount of waste deposited was about 23,000 tonnes. The MSW (Municipal Solid Waste) was comprised of 35.2% food waste, 11.6% paper and cardboard, 4.1% textiles, and 18.4% plastics.

The LandGem model assumes that methane generation can be predicted by a simple first order exponential decay:

$$Q_{CH_4} = \sum_{i=1}^{N} \sum_{j=0.1}^{1} k L_0 \left(\frac{M_i}{10} \right) e^{-k t_{ij}} \qquad 11)$$

For a full definition of symbols, see the LandGem User Guide [35].

The model has two parameters, L_0 and k.

$L_0 = DOC \times DOC_f \times F \times (16/12) \times MCF$ 12)

DOC=Degradable Organic Carbon.

DOC = 0.4 (A) + 0.17 (B) + 0.15 (C) +0.3 (D) 13)

where A is the fraction of Municipal Solid Waste (MSW) that is paper and textile wastes, B is the fraction of garden/park wastes or another non-food organic degradable waste, C is the fraction of food waste and D is the fraction of wood and straw wastes.

For the case of the Bahrain landfill, A=0.157, B=0.028, C=0.352, and D=0.018, i.e., the total fraction of decomposable waste = 0.555. The fraction of plastic film and other plastics in the MSW was 0.184. Per the US EPA model this material does not decompose, as it should not, per the stoichiometric equations for anaerobic decomposition (Equations 9 and 10), because petrochemical plastics such as polyolefins or polystyrene have no chemical path for anaerobic degradation. Other non-gradable components include metal and glass.

DOC_f = the fraction of dissimilated DOC. Coscuner, et al. [34] calculated DOC_f as a function of assumed landfill temperature using the formula of Alexander, et al. [35]. They used a value of 0.77.

MCF = molecular weight correction factor = (16 g/mol CH4)/(12 g/mol C).

The EPA LandGem model predicts an exponential decline in methane generation following landfill closure. Approximate CO_2 generation can be predicted assuming the biogas is 50% CH_4 and 50% CO_2 per the stoichiometry of anaerobic degradation. Then, the mass of the biomass that has been degraded can be approximated as the sum of the mass of CH_4 and CO_2 generated via **Eqn. 10**.

LandGem moldel calculations for the cases in this manuscript are provided in **SI.4**. The LandGem model provided an exact match to the methane formation reported by Coscuner, et al. for L_0=90.59 m^3/Mg and k=0.012. (Coscuner, et al. used a value of 0.0123 for k). The LandGem output for CH_4 formation through 127 years after closure were refit to an exponential decay, and then extrapolated to 700 years after closure. The cumulative CH_4 make reaches an asymptote representing a cumulative fraction of degradable mass that has decomposed of 40.9%. Note that this calculation assumes 55.5% of the total placed waste is degradable.

The model was used to estimate the fraction of switchgrass that would decompose in a normal landfill at the asymptote. Waste placement was assumed to be the same as in the Bahrain landfill example, except the biomass is assumed to be 100% degradable straw. Thus, DOC = 0.3 x D = 0.3 x 1 = 0.3.

Revised IPCC Good Practice indicate that the value of k calculated from the formula of Alexander et al. [35] is too high and suggest a value of 0.5-0.6 if the waste contains biomass with a substantial fraction of lignin [36]. There is no chemical path for lignin to decompose, and the fraction of biomass that does not decompose is higher than the lignin content due to cross linking of lignin to cellulose. Thus, to model switchgrass decomposition, a value of DOC_f of 0.5 was assumed, yielding L_0=140 m^3/Mg. EPA Guidelines provide an estimation of k based on average rainfall at the landfill site [37]. To investigate the effect of average rainfall, switchgrass decomposition was modelled with k=0.05 (EPA CAA Conventional default); k=0.012 (Arid region); and k=0.102 (High rain region, based on the average rainfall for Malasia). Estimates for k as a function of average rainfall in US states and various countries are provided in **SI.4**. Calculations for the Bahrain landfill waste placement are provided in **SI.2**. LandGem calculations for the degradation of 100% switchgrass are provided in **SI.4**. **Fig. 9** it the estimated methane make from switchgrass degradation as a function of year after landfill closure for varying k. It shows that a higher k leads to faster degradation and a higher maximum generation rate at early years after closure.

However, as shown in **Fig. 10**, the predicted cumulative asymptotic fraction of the switchgrass predicted to decompose is essentially independent of k, at about 35%. The sensitivity of k to average rainfall indicates the necessity of water to initiate biomass decomposition. We propose drying the switchgrass and leaves prior to placement as one way to prevent decomposition. It is well known that hay can be stored in barns for periods of years without undergoing degradation or mold formation if it is properly dried. Is 35% decomposition too high? No. Biogas collection, removal, and sequestration of the CO_2 in the biogas (CCS) would still be possible if public policy and a carbon tax were in place to support that investment. Do we believe that landfills can be designed to reduce switchgrass decomposition below 35%? Yes. Test landfills should be constructed to test ideas.

6. The Cost of CCS for an SRM Hydrogen Plant and Coal and Natural Gas Power Plants

Costs for CCS for several technologies will be calculated in this section for comparison to the cost of CCS for biomass growth and sequestration in landfills.

There is much recent interest related to hydrogen production because hydrogen is a carbon-free fuel. The steam reforming of methane (SRM) has been practiced for almost 100 years as a means of producing hydrogen for refineries and chemical plants.

A schematic of a typical SRM hydrogen plant is provided in **Fig. 11**. Feed gas is preheated and pretreated to remove sulfur. The pretreated gas is mixed with steam (and some recycled hydrogen product) and reformed over a catalyst at high temperature. For small hydrogen plants, the reforming "reactor" is catalyst packed right into furnace tubes. The feed is first preheated by heat exchange with hot flue gas. Heat is recovered from the hot flue gas by generating steam. The hot effluent from the steam reforming reactor is cooled and passed to water-gas shift reactors. Equilibrium conversion to CO_2 and H_2 in the water-gas shift reactors is favored by low temperature. Water-gas shift conversion is limited by thermodynamics, which favors higher conversion at lower temperatures. Thus, the shift may be done in two steps. A first high temperature shift reactor is used to provide faster reaction kinetics. A second low temperature shift reactor is used as a trim reactor to provide high conversion.

Some hydrogen atoms in the methane are converted to water, which is largely removed by cooling and separation in a condensate drum.

CO_2 separation and hydrogen purification and separation are shown as a block (Hydrogen Purification) in **Fig. 11**. Within that block, hydrogen separation and purification are commonly done by a pressure swing adsorption (PSA) unit. The PSA unit produces the purified hydrogen product and a PSA tail gas that contains unreacted CH_4, unrecovered H_2, unconverted CO, and CO_2. The CH_4, H_2, and CO give the tail gas a heating value. This gas is burned in the reformer furnace. However, since the reforming reaction is so endothermic, additional natural gas is needed and burned, generating additional CO_2.

CO_2 is typically removed from the PSA tail gas by absorption in an amine solution followed by CO_2 removal from the rich amine solution in a stripper distillation column. CO_2 stripping is very energy intensive. The stripped CO_2 is compressed and cooled to liquify for export.

Note that steam is generated in multiple places in the process. That steam can be used to turn turbines to generate electricity in a combined cycle power plant, in which the hydrogen product can be burned to produce more steam and more power, or it can be exported for use in a refinery or chemical plant or elsewhere (the basis for a hydrogen economy). In a hydrogen plant dedicated to H_2 production for a refinery or chemical plant, net steam is produced, that must find a home. Receiving value for export steam is very important for the economics of these units and makes CCS site specific.

Fig. 11 shows the capture of CO_2 produced in the SRM and water-gas shift reactors. However, that is only a portion of the CO_2 generated in the entire process. **Fig, 12** is a block flow diagram for the overall SRM hydrogen plant that shows three different positions where CO_2 can be captured: 1) after the water-gas shift reactors and ahead of the PSA unit; 2) from the PSA tail gas; or 3) from the reformer furnace vent gas. Since the process is so net endothermic, CO_2 generated by additional natural gas required for the reformer furnace accounts for about 40% of the total CO_2 generated. Thus, recovery from the furnace vent gas is the only position that can make SRM nearly CO_2-free, and even at that position total CO_2 recovery is typically only about 90%. Thus, an SRM hydrogen plant will continue to produce some CO_2 generated from fossil fuel that will be released to the atmosphere.

IEA provided estimates for H_2 production cost for an SRM with and without CCS for various world regions [38]. H_2 cost is broken down into natural gas, CAPEX and OPEX costs. These costs are from an engineering study performed by Foster-Wheeler [39] for a large 100,000 Nm^3/hr SRM H_2 plant. For reference, the world's five largest single train SRM plants range from 151,000 Nm^3/hr to 240,000 Nm^3/hr.

The modeled plant produces 100,000 Nm^3/hr H_2 = 9.0 t/hr H_2, and 38.1 t/hr CO_2 (total in the reformer

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 2 November 2021 doi:10.20944/preprints202106.0212.v4

furnace flue gas). The IEA incremental CAPEX (with CCS vs. no CCS) is \$0.26/kg H_2 and the incremental OPEX is \$0.24/mt H_2, which correspond to \$61/mt CO_2 and \$57/t CO_2 respectively, assuming 100% CO_2 recovery. Thus, total cost for CCS is \$118/t CO_2 including transportation and underground storage. Details for these calculations are provided in **SI.3.** Economics of scale mean that CAPEX costs would be larger for smaller units.

The costs for carbon capture and sequestration (CCS) for a supercritical coal and natural gas combined cycle power plants can be better defined from cost elements provided by the US EIA [40]. Detailed calculations for CCS from these plants are also provided in **SI.3.** Costs are site specific. The cost for CCS for a supercritical coal power plant is calculated to be \$91/mt CO2 for a supercritical coal power plant and \$83/mt CO_2 for a natural gas combined cycle power plant for a Texas location, based on a 6% PI, 15 yr capital charge. This includes transportation and storage in a nearby saline aquifer.

These may be conservative estimates. Roussanaly et al. indicate that the calculation of the true cost of CCS is complicated and depends on a number of site and project specific items, such as the source of energy for CO_2 stripping from the amine (electric steam boiler versus natural gas) [41]. The additional CO_2 generated by the unit generating heat for stripping is often not included when calculating the cost of CCS by others.

It is worth noting that to date, CCS for coal-fired power plants has only been implemented on a commercial scale at two locations world-wide, one in Texas at Petra Nova and one in Canada. The Petra Nova project added a 240-megawatt (MW) carbon capture system to Unit 8 (654 MW capacity) of the existing W.A. Parish pulverized coal-fired generating plant representing about 37% of Unit 8’s emissions, which are diverted through a flue gas slipstream [42]. The US EIA web page for the project [42] illustrate some of the challenges for the project, which include: 1) the size of the equipment needed for CO_2 capture, and 2) the need for a separate co-gen unit to supply steam heat for separating the captured CO_2 from an MEA solvent. While it operated for several years, the Petra Nova project closed in February 2020 due to poor economics [43]. The captured CO_2 had been sent for tertiary oil recovery. The project demonstrated that CCS technology is possible on a commercial scale. However, its closure also indicated that CCS technology will not move forward without government support in the form of substantial tax credits and a mandated cost of carbon.

Laura Martin of the EIA provided estimates for CO_2 transportation and storage in a saline aquifer for different regions in the US in a private email to J. Amelse dated July 1, 2021. These are included in **SI.3.** The higher cost for CO_2 transportation and storage in a saline aquifer in the coal regions of Illinois or Pennsylvania can add another \$17 or \$33/mt CO_2 respectively. Capital and delivered natural gas costs are also higher in those regions.

It remains to be seen what actual costs for CCS will be when large projects, including pipelines and storage in aquifers are delivered.

7. The Cost of CCS for Biomass Sequestration in a Landfill

The cost of CCS for biomass sequestration will be comprised of two components: 1) the cost of harvesting leaves, or the cost of growing and harvesting cultivated biomass such as switchgrass; and 2) the cost of landfilling.

Growing and landfilling switchgrass will be considered first. Farm-Energy estimated the cost of producing switchgrass in the US Upper Midwest at \$72/mt) [44]. This assumes a conservative switchgrass yield of 3.5 ton/acre. New varieties of switchgrass are being developed that could increase yield to 6-9 ton/acre, which would lower production cost to about \$28-42/mt.

Statistica indicates that the 2020 cost to landfill varies across the US from about \$45/mt in the South Central region to about \$81/mt in the Pacific region with a US average of about \$61/mt [45]. Thus, the cost to grow and sequester switchgrass could be as low as about \$73/mt in the South, making it a low-cost method of Direct Air Capture of CO_2.

The cost for harvesting and bailing hay is well known [6], and thus the cost of producing switchgrass should be comparable and accurate. The cost for harvesting tree leaves would have more uncertainty. Harvesting leaves from established forests would have no growing costs, and thus, zero net raw material cost. However, harvesting costs would be expected to be higher for leaves due to lower compacted density. The density of hay is about 150-250 kg/m^3 [46], compared to a density of about 113 kg/m^3 for compacted leaves. The latter value is from a private email dated April 27, 2021, from the Commissioner of Streets and Sanitation for the city of Batavia, Illinois.

How much CO_2 capture potential could growing and sequestering switchgrass provide? The following calculations use the ratio of CO_2/CH_2O MW of 44.01/30.03, a switchgrass yield of 9 tonne/acre, and assumes 80% permanent capture in an unmodified landfill, i.e., decomposition is limited to 20%. Corn accounts for more than 95% of total feed grains in the US. In 2019, greater than 90 million US acres of corn were planted [47]. If the 40% of that crop devoted to bioethanol were replanted with switchgrass and sequestered, the CO_2 capture potential is 380 Mt/yr. In 2019, 89.1 million acres of soybeans were planted in the US [48]. If half of that land were devoted to switchgrass, that CO_2 capture potential would be another 470 Mt/yr. In addition, range and pastureland accounts of 27% of total land in the contiguous US, or 528 million acres [49]. If 30% of that land were devoted to switchgrass, the CO_2 capture potential would be 1.7 Gt/yr. These calculations are for the US. The world potential is enormous, and clearly many Gt/yr.

8. Secondary Issues and Practicality

The main secondary issues include:

1) For leaf gathering, the main issue is accessibility. While theoretically, there are enough leaves in the world to achieve Net Zero CO_2 if they were gathered and sequestered, trees are distributed with many in remote areas that are not accessible. Reforestration is a popular current topic. New forests should be planted structurally with leaf gathering in mind.
2) Resupply of nutrients pulled from the ground is another issue. As noted above, plants receive all of

their carbon from CO_2 in the air via photosynthesis. However, the enzyme that catalyzes photosynthesis required nitrogen and phosphorous. For trees in mature forests, those can come from decomposition of leaf and dead trees. In addition to N, P, and K, there are other micronutrients such as B, Fe, etc. There is nothing in the list of nutrients that cannot be supplied by external fertilization with a proper mix. Note that natural forests are sustainable without external fertilization. There are nitrogen fixing plants, such as soybeans. Crop rotation between corn and soybeans is practiced reducing the need for external fertilization. Also, nitrogen fixation is carried out naturally in soil by microorganisms termed diazotrophs that include bacteria such as Azotobacter and Archaea. Perhaps research and commercial development of these bacteria could lessen fertilizer requirements.

3) For growing switchgrass on US western pastureland, a secondary issue will be water, as this area continues to be under severe drought conditions.

Would it be practical to achieve full Net Zero CO_2 (36 Gt/yr CO2 removal) by sequestering tree leaves and growing and sequestering high yield switchgrass? The answer is likely not. However, these methods can play an important role in supplementing energy conservation, renewable energy, and CO_2 sequestration from existing and future large point sources. CO_2 removal on a Gt/yr should be possible.

The issue of practicality will be addressed in two ways: 1) The volume of leaves and switchgrass that would need to be sequestered to pull 1 Gt/yr CO_2 from the air will be compared to the volume of coal that is currently removed from the ground each year; and 2) The practicality of pulling an equivalent amount of CO_2 from the air by sequestering biomass will be compared to the amount of CO_2 that may be removed by low-carbon hydrogen production installed, announced and in the Sustainable Development Scenario of the IEA for the period 2010-2030 [50].

Historical data provided by IEA indicates that world annual coal production peaked at about 8 Gt in 2013, and after a dip to about 7.3 Gt in 2016 recovered to about 7.9 Gt in 2019 [51]. Using 8 Gt/yr and an average compacted coal density of 881 kg/m^3 (the average-e for anthracite and bituminous) [52], that is about 9 billion m^3/yr. The average compacted density of leaves is about 113 kg/m^3. The ratio of coal to leaf density is about 7.8. Thus, burying 1 Gt/yr of leaves would occupy about the same volume as the amount of coal mined in 2013. Remember that the amount of CO_2 removed from the air for burying 1 Gt leaves or other biomass is about (44.01 gm/mol CO_2/30.03 gm CH_2O) = 1.47 CO_2 equivalent. Thus, achieving 1 Gt/yr reduction of CO_2 by burying leaves seems within the realm of possibility. The density of large round hay bales is about 177 kg/m^3 [53], and switchgrass density should be about the same. Thus, the ratio of coal density to hay density is about 5. Thus, burying 1 Gt/yr of switchgrass (1.47 Gt/yr CO_2 removal) would require about 63% of the volume of coal mined in 2013.

IEA has provided a recent update of low-carbon hydrogen production projects, installed, announced and in the IEA Sustainable Development Scenario, for the period 2010-2030 [50]. Through 2019, only about 0.4 Mt/yr low-carbon H_2 has been installed, total announced projects through 2023 are only 1.4 Mt/yr, and total in the plan through 2030 are only 7.9 Mt/yr H_2. Thus, the equivalent amount of CO_2 capture for low carbon H_2 plants in the plan through 2030 is only 33.4 Mt/yr CO_2. While there are high hopes for a hydrogen economy contributing to the reduction of CO_2 emissions, this is nowhere near the 36 Gt/yr that needs to be eliminated, and nowhere near the potential for CO_2 removal by sequestration of on-purpose switchgrass and tree leaves.

9. Final Comments

Here are some final comments regarding the proposed permanent biomass sequestration as a means of Direct Capture removal of CO_2 already in the atmosphere.

- Theoretically can it achieve Net Zero CO_2? Yes, there are enough tree leaves, and on-purpose growth of switchgrass can achieve Net Zero on its own independent of other technologies.
- Is it technically sound? Yes. Landfills can be designed to prevent biomass degradation to CO_2 and/or methane. In fact, encouraging degradation in bioreactor landfills is actually a more difficult problem.

- Is it actionable? Yes. It could be put into practice in the timeframe required (before 2030-2050).
- Are there secondary issues? Yes: 1) Designing new managed forests with leaf collection in mind; 2) Soil nutrient replacement; 3) Designing secure leaf landfills with no or minimal decomposition and leakage; and 4) water for switchgrass growth in dry areas. However, these issues can be addressed by gathering the right group of people, i.e., experts in forestry, soil chemistry, landfill management.
- The potential for carbon capture via tree leaf collection and growing and sequestering switchgrass is enormous, numerous Gt/yr, as shown in Sections 4 and 8.
- Is it still a daunting problem? Yes. To achieve Net Zero CO_2 for the current 36 Gt/yr of CO_2 using this technique alone would require sequestering an enormous amount of material. Of course, this would be reduced, perhaps in half, by energy conservation, renewable energy, CO_2 sequestration from large point sources, other carbon capture innovations, etc. Even at incomplete implementation, it can play an important role in reducing net CO_2 to the atmosphere.
- Can any of the other current proposed technologies achieve Net Zero CO_2 on their own? No.
- How would biomass landfill projects be funded? CO_2 sequestration will be expensive. That is reality. It will take a government mandated cost of carbon and tax incentives. The business model for this proposal would be the following. Corporations would invest in the landfills and leaf or biomass growth and collection. Farmers would grow high yield crops for carbon sequestration and would be compensated for their efforts. Carbon credits would be sold to recover investments.

ACKNOWLEDGMENTS

Amelse received a Ph.D in Chemical Engineering from Northwestern University, Evanston, IL USA. He worked for Amoco Chemical Company R&D (BP Amoco Chemical Company Petrochemicals Technology), Naperville, IL USA, for 35 years, mainly on paraxylene catalyst and process technology. He retired in April 2017 and joined CICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Portugal as Invited Principal Investigator to continue collaboration on the characterization of molecular

sieve catalysts and adsorbents via Solid State NMR, work started while at BP. He has published numerous papers and is co-inventor on 17 issued or pending patents. He was recently extended a 3-year unpaid position as Invited Associate Professor, so he can continue to teach on-line and collaborate on several projects following his return to the US.

Paul Behrens received a Ph.D. in Chemical Engineering from the University of Delaware. He joined Amoco Chemical Company R&D and spent 28 years there, supporting numerous chemical processes, including para-xylene, PTA, polybutene, 2,6-naphthalene dicarboxylic acid, and efforts to commercialize cellulosic bioethanol. He continues as an independent consultant with expertise in process modeling, design, and economics. Since his semi-retirement, he purchased a farm near Indianapolis, IN where he grows hay.

This article was developed as an independent contribution. As such, the authors declare no organizational funding for this article.

CORRESPONDING AUTHOR

JAmelse@UA.Pt, AmelseJeff@Gmail.com

SUPPLEMENTAL INPUT

Available from the corresponding author upon request.

REFERENCES

[1] R. Lindsey, Climate Change: Atmospheric Carbon Dioxide | NOAA Climate.gov, 2020.

[2] Climeworks, https://www.climeworks.com. Accessed May 18, 2021.

[3] D.W. Keith, G. Holmes, D. St. Angelo, and K. Heide, Joule 2, 1573-1594, 2018. https://doi.org/10.1016/j.joule.2018.05.006.

[4] CNBC, Money Is Pouring Into Carbon Capture Tech, But Challenges Remain - Bing video

[5] IEA, "Building the Cost Curves for CO_2 Storage: North America," Report 2005/3, 2005. Available at Microsoft Word - USA Cost curves Overview - revised.doc (ieaghg.org)

[6] K. Painter, "Costs of Harvesting Hay: Does it Pay to Put Up Your Own," Costs of harvesting hay: Does it pay to put up your own? - Progressive Cattle.

[7] US Energy Information Authority (EIA), "Annual Energy Review," 2020. https://www.eia.gov/totalenergy/data/annual/

[8] BP, bp Statistical Review of World Energy 2020

[9] EIA, "Energy Facts Explained," 2017. Current version at: https://www.eia.gov/energyexplained/us-energy-facts/

[10] EIA, "Annual Energy Outlook 2020," https://www.eia.gov/outlooks/aeo/ Accessed Sept 9, 2020.

[11] EIA, "Petroleum and Other Liquids, International - U.S. Energy Information Administration (EIA) (2021). Accessed July 12, 2021.

[12] EIA, "U.S. Sales of Distillate Fuel Oil by End Use," http://www.eia.gov/dnav/pet/pet_cons_821dst_dcu_nus_a.htm Accessed May 18, 2021.

[13] USDA, "Feed Grains Data: Yearbook Tables," 2020. https://www.ers.usda.gov/data-products/feed-grains-database/feed-grains-yearbook-tables.aspx

[14] Katzen, R., Moon, G.D., Jr., Kumana, J.D., US Patent No. 4,217,178, Distillation System for Motor Fuel Grade Anhydrous Ethanol, Aug. 12, **1980**. Available at https://patentimages.storage.googleapis.com/5f/91/35/16633397cd2fe4/US4217178.pdf

[15] Kwiatkowski, J. R. (2006) A. J. McAloon, A.I., Taylor, F., Johnston, D.B., Modeling the process and costs of fuel ethanol production by the corn dry-grind process. (cabdirect.org) *Industrial Crops and Products* **2006**, 23 288–296. DOI : 10.1016/j.indcrop.2005.08.004.

[16] C. Hettinger , and T. Lisi, "$208 million project stores ADM's carbon deep beneath Decatur | Local | herald-review.com," Herald & Review, Oct 1, 2017.

[17] Globe Newswire, Green Plains Announces Carbon Sequestration Partnership (globenewswire.com), Feb. 18, 2021.

[18] Valero Energy Corp., Ethanol Producer Magazine – The Latest News and Data About Ethanol Production www.ethanolproducer.com/articles/18070/valero-blackrock-partner-with-navigator-on-ccs-project. , March 17, 2021.

[19] Sandia Labs News Release, Sandia National Laboratories: News Releases : Biofuels can provide viable, sustainable solution to reducing petroleum dependence, say Sandia researchers, 2009.

[20] S. Retka Schill," "Zero to 10 Million in 5 Years, *Ethanol Producer Magazine*, June 26, 2018. Available at: Ethanol Producer Magazine – The Latest News and Data About Ethanol Production

[21] EIA, "Monthly Biodiesel Production Report," https://www.eia.gov/biofuels/biodiesel/production/ Accessed May 18, 2021.

[22] US Department of Agriculture (USDA), "US Bioenergy Statistics," https://www.ers.usda.gov/data-products/us-bioenergy-statistics/

[23] USAfacts.org, How many electric cars are on the road in the United States? (usafacts.org) Accessed May 18, 2021.

[24] J. A. Bassham, photosynthesis | Definition, Formula, Process, Diagram, Reactants, Products, & Facts | Britannica, 2020.

[25] J. Carson, How Much Carbon Can Soil Store | Fact Sheets | soilquality.org.au 2020.

[26] EPA, National Overview: Facts and Figures on Materials, Wastes and Recycling | US EPA, 2020.

[27] E.G. McPherson, N.S. van Doorn, and P.J. Peper, USDA Urban Tree Equations.pdf

[28] Crowther, T., Glick, H., Covey, K. *et al.* Mapping tree density at a global scale. *Nature* **525,** 201–205 (2015). https://doi.org/10.1038/nature14967.

[29] GreenBlizzard, "How Many Trees in the US ?," 2016. Available at: http://greenblizzard.com/2015/09/28/how-many-trees-in-the-u-s/

[30] Agency for Toxic Substances and Disease Registry, "Landfill Gas Primer - An Overview for Environmental Health Professionals, Chapter 2: Landfill Gas Basics," 2001. https://www.atsdr.cdc.gov/HAC/landfill/html/ch2.html

[31] S. Datta and L. Eastes, Biodegradation in Municipal Solid Waste Landfills, Geoenvironmental Engineering, 2015. Available at: Biodegradation in Municipal Solid Waste landfills | Geoengineer.org.

[32] National Council for Air and Stream Improvement, Technical Bulletin No. 872 Critical Review of Forest Products Decomposition in Municipal Solid Waste Landfills (ncasi.org).

[33] Y. Chen, J.J. Cheng, K.S. Cramer, "Inhibittion of anaerobic digestion process: A review," *Biosource Tech.*, 99, 4044-4064. https://doi.org/10.1016/j.biortech.2007.01.057

[34] G. Coskuner, M. S Jassim , N. Nazeer, and G. H Damindra, "Quantification of landfill gas generation and renewable energy potential in arid countries: Case study of Bahrain, Waste Management & Research, vol. 38, 10: pp. 1110-1118, 2020. https://doi.org/10.1177/0734242X20933338

[35] A. Alexander C. Burklin, and A. Singleton, Landfill Gas Emissions Model (Land GEM) Version 3.02 User's Guide: May 2005 (epa.gov), 2005.

[36] Chapter 5 Waste, IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Available at: 5_Waste-1 Includes DOC formula.pdf

[37] USEPA, Direct Emissions from Landfilling Municipal Solid Waste. Climate Leaders Greenhouse Gas Inventory Protocol. Washington, DC: U.S. Environmental Protection Agency Office of Research and Development, 2004.

[38] IEA, "The Future of Hydrogen – Report Prepared for the G20, Japan," 2019. Available at The Future of Hydrogen (windows.net)

[39] IEA, IEAGHG Technical Review 2017-TR3, Reference Data and Supporting Literature Reviews for SMR Based Hydrogen Production with CCS, 2017. Available at 2017-TR3.pdf (ieaghg.org)

[40] EIA, Cost and Performance Characteristics of New Generating Technologies, Annual Energy Outlook 2021 (eia.gov), February, 2021.

[41] S. Roussanaly, N. Berghout, T. Fout , M. Garcia, S. Gardarsdottir, S. Mohd Nazir, A. Ramirez, E. S. Rubin, Towards improved cost evaluation of Carbon Capture and Storage from industry, International J. of Greenhouse Gas Control, 106, 103263, 2021. Available at Towards improved cost evaluation of Carbon Capture and Storage from industry - ScienceDirect

[42] EIA, Petra Nova is one of two carbon capture and sequestration power plants in the world - Today in Energy - U.S. Energy Information Administration (EIA), October 21, 2017.

[43] C. Anchondo and E. Klump, TECHNOLOGY: Petra Nova is closed: What it means for carbon capture -- Tuesday, September 22, 2020 -- www.eenews.net (house.gov), E&E News, September 22, 2020.

[44] Farm-Energy, The Economics of Switchgrass for Biofuel – Farm Energy (extension.org) 2019.

[45] Statistica, • Cost to landfill MSW by U.S. region 2020 | Statista, release date, February, 2021.

[46] DairyNZ, "Density and Storage of Feeds," Available at Density and storage of feeds - DairyNZ.

[47]USDA, "Feedgrains Sector at a Glance." Available at USDA ERS - Feedgrains Sector at a Glance.

[48] USDA, USDA ERS - Related Data & Statistics

[49] USDA, Range & Pasture | NRCS (usda.gov).

[50] IEA, Low-carbon hydrogen production, 2010-2030, historical, announced and in the Sustainable Development Scenario, 2030 – Charts – Data & Statistics - IEA. Last updated 9 JUN 2020.

[51] IEA, “World total coal production, 1971-2019 provisional,” https://www.iea.org/data-and-statistics/charts/world-total-coal-production-1971-2019-provisional Last Updated 9 JUN 2020,

[52] Brabender Technolog, “Reference Information – Ingredient Bult Density Table,” Document: 1500-C01-2, April 2003. Available at Bulk Density Table (sawyerhanson.com)

[53] Hayforks.com, “How Much does a Bale of Hay Weigh?” 2020. https://hayforks.com/blog/how-much-does-a-bale-of-hay-weigh

FIGURES

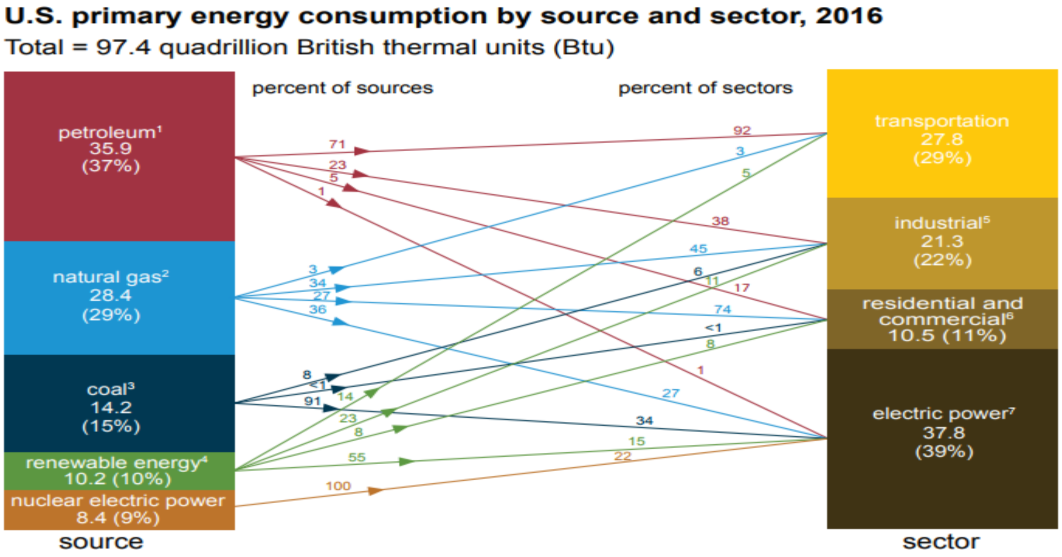


Fig. 1. US Primary energy consumption by source and sector, 2016 Source: EIA (2017) [9]. All rights reserved.

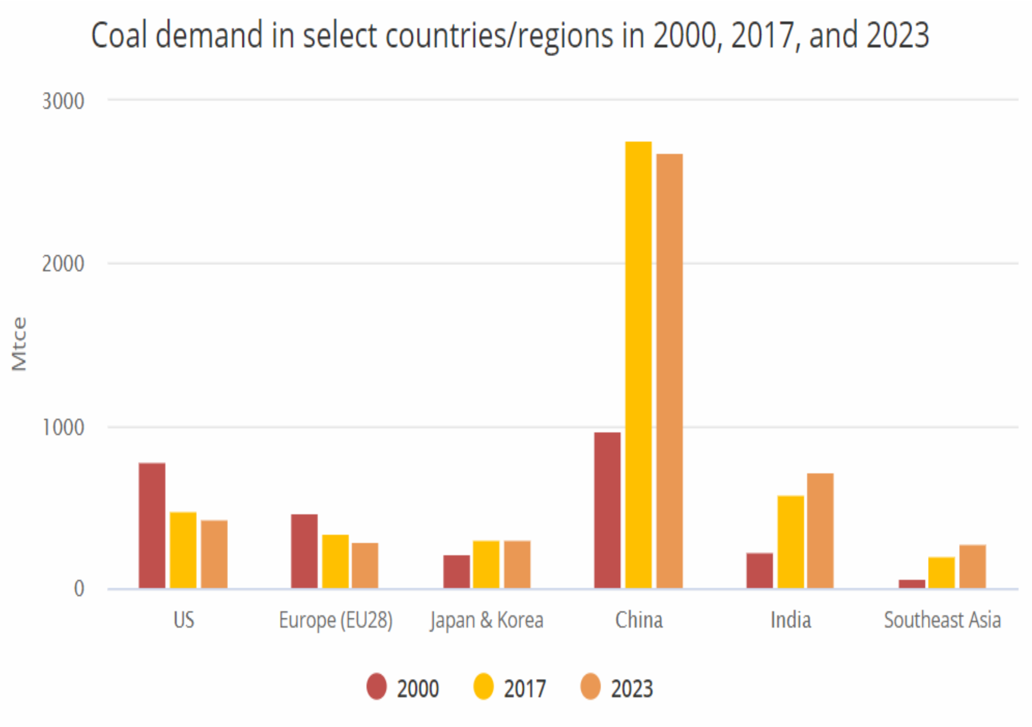


Fig. 2. Coal demand in select countries/regions
Data Source: (EIA, 2017). All Rights Reserved. [9]

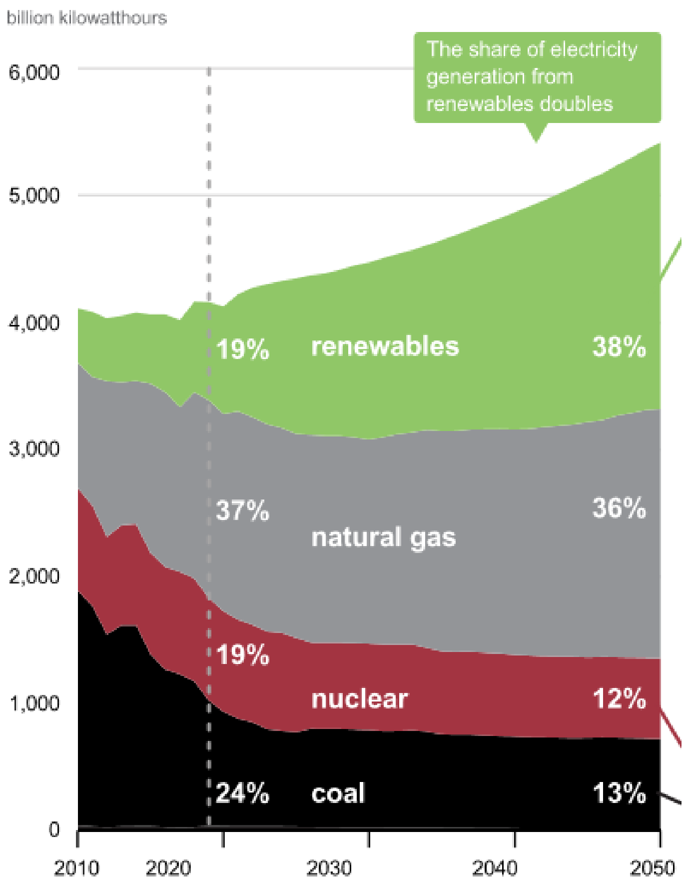
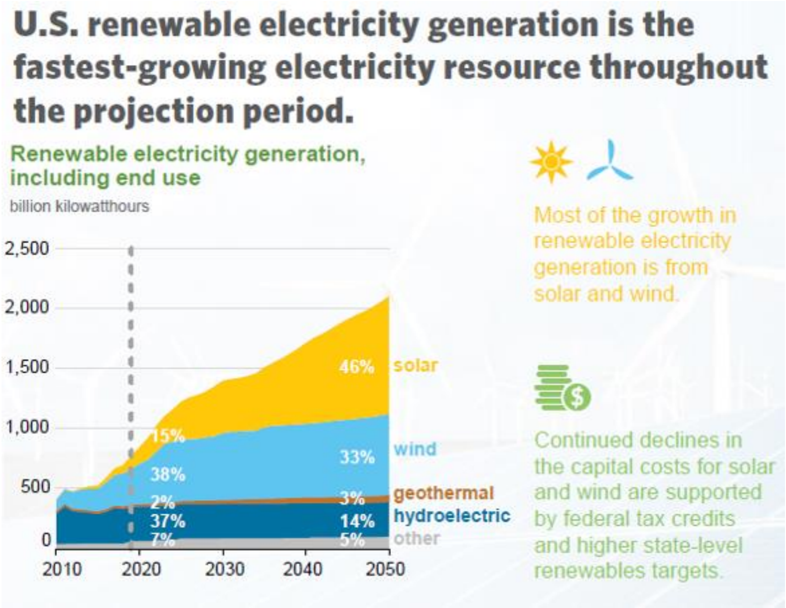


Fig. 3. Shift in all sources of energy for electricity.
Source: (EIA, 2020). All Rights Reserved. [10]


U.S. renewable electricity generation is the fastest-growing electricity resource throughout the projection period.

Most of the growth in renewable electricity generation is from solar and wind.

Continued declines in the capital costs for solar and wind are supported by federal tax credits and higher state-level renewables targets.

Fig. 4. Shift in source of renewable energy for electricity.
Source: (EIA, 2020). All Rights Reserved. [10]

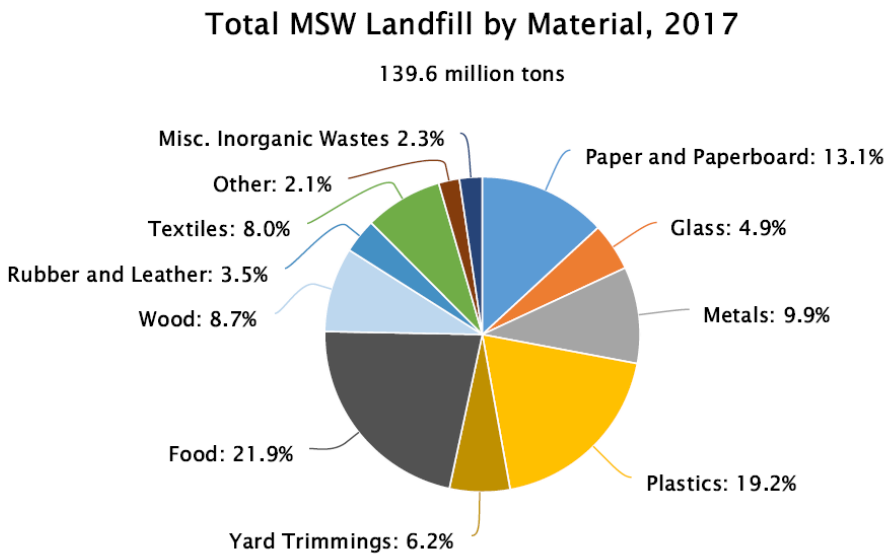


Fig. 5. US 2017 Municipal and Yard Waste Landfilled
Source: (EPA, 2020) [26].

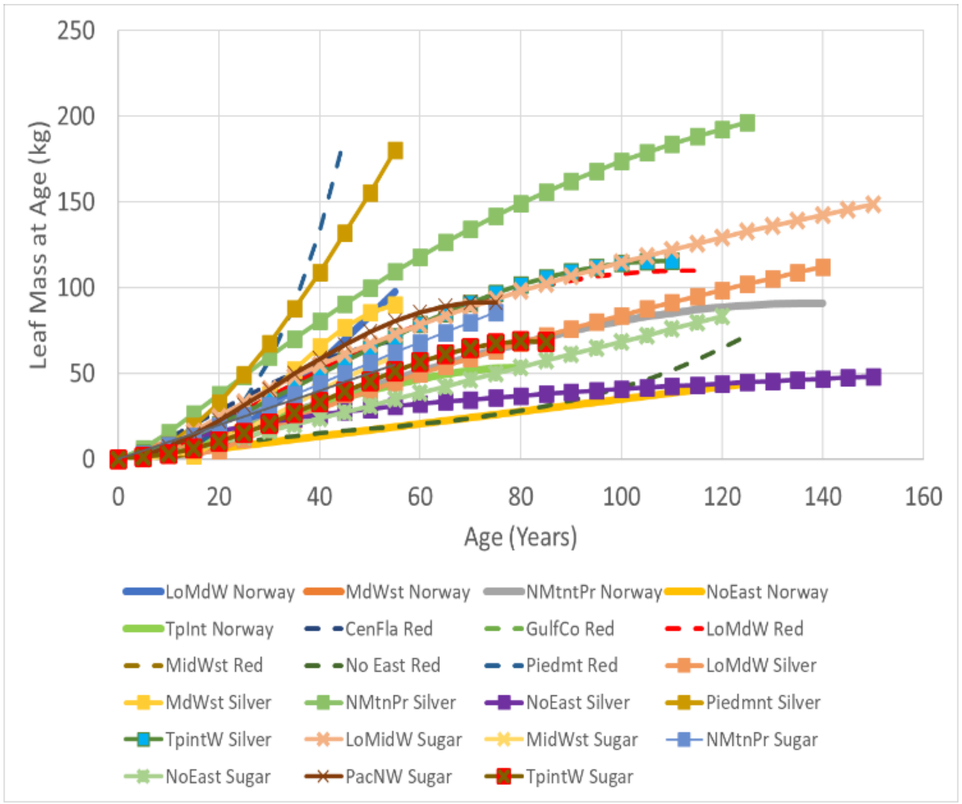


Fig. 6. Yearly dry leaf biomass generation by some maple tree species in various regions of the US
Source: McPherson, van Doorn, and Peper (2016) [27].
The US regions include: LoNdWst=Lower Midwest; MidWst=Midwest; NMtnPr=North:
No East = North East; CenFla=Central Florida; GulfCo=Gulf Coast; Piedmt=South.

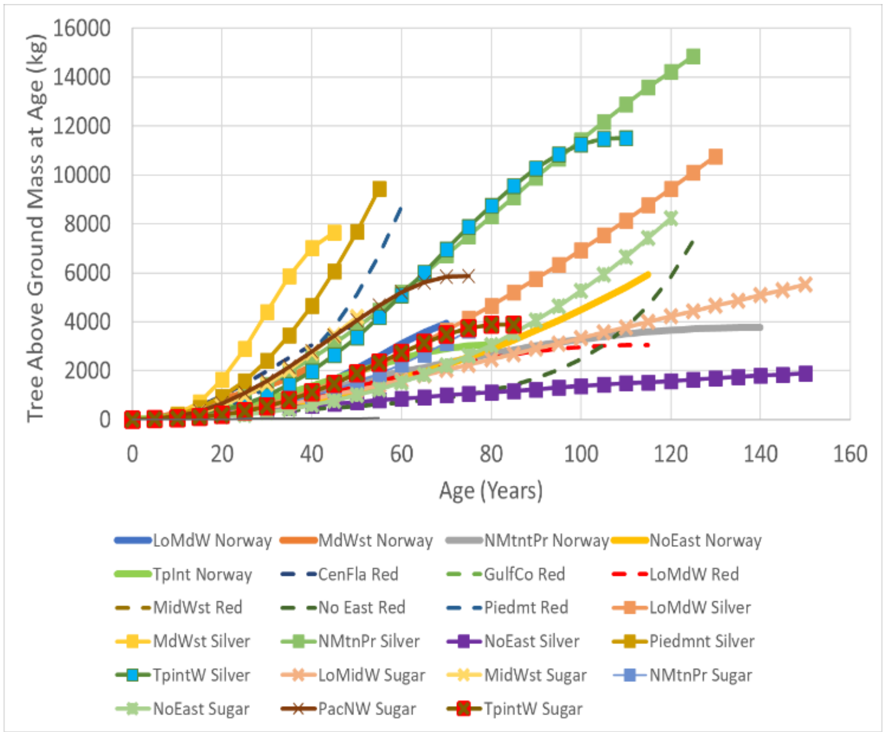


Fig. 7. Above ground biomass for some Maple tree species in various regions of the US. Source: McPherson, van Doorn, and Peper (2016) [27].

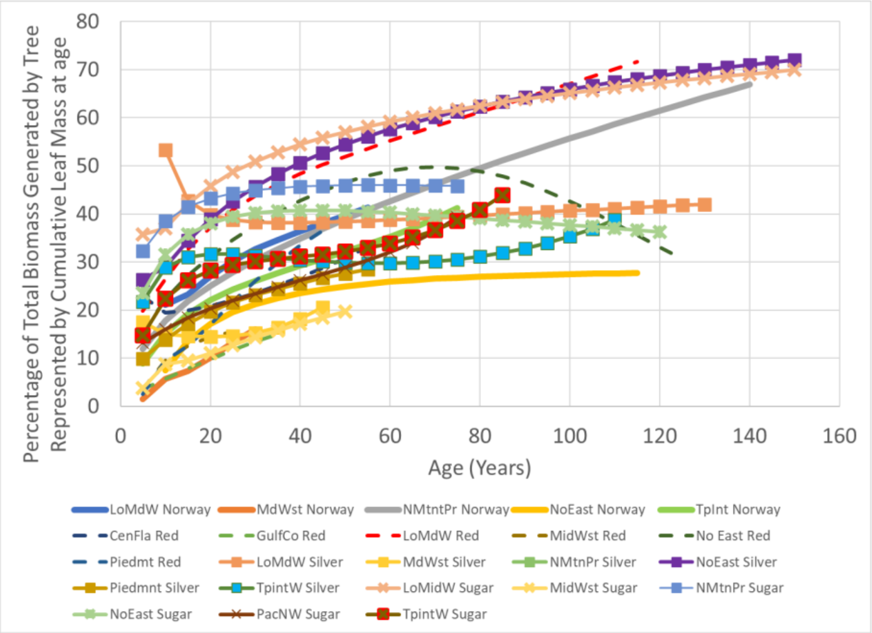


Fig. 8. Percentage of total biomass generated by a tree represented by cumulative lead mass at age for various species of Maple trees at various locations in the US.

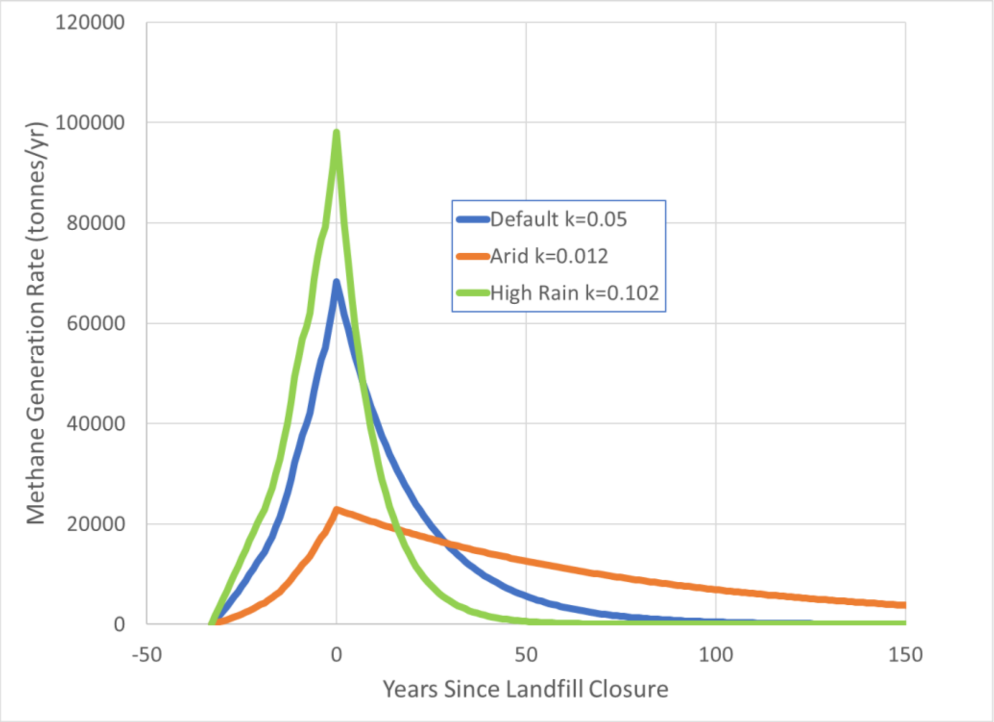


Fig. 9. EPA Landfill Gas Emissions Model (LandGEM) Prediction of Methane Make as a Function of Years After Landfill Closure

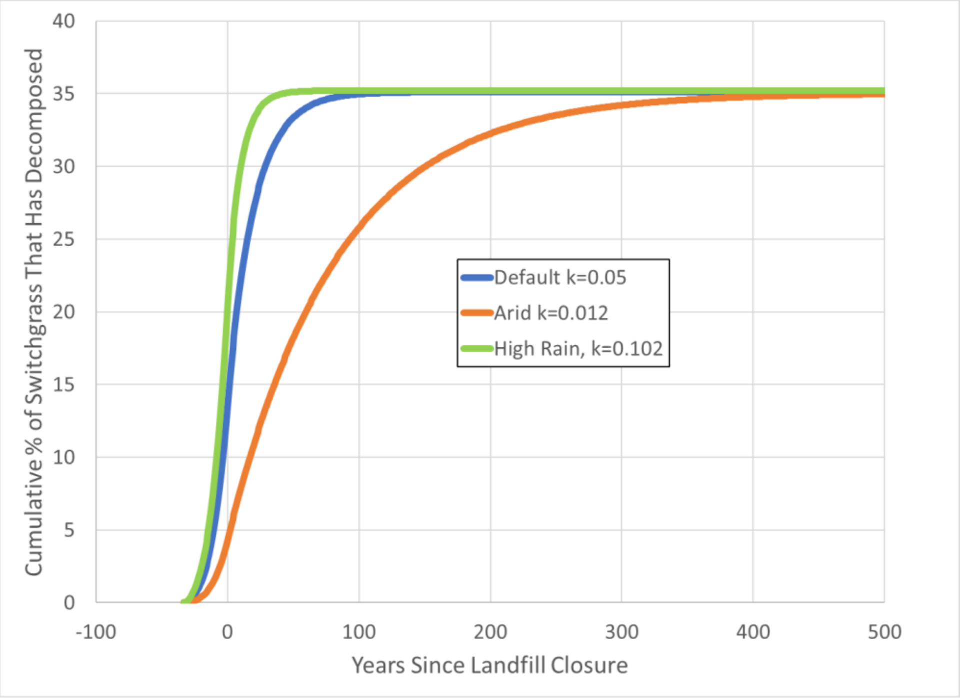


Fig. 10. EPA Landfill Gas Emissions Model (LandGEM) Prediction of the Cumulative Fraction of Switchgrass Decomposed as a Function of Years After Landfill Closure

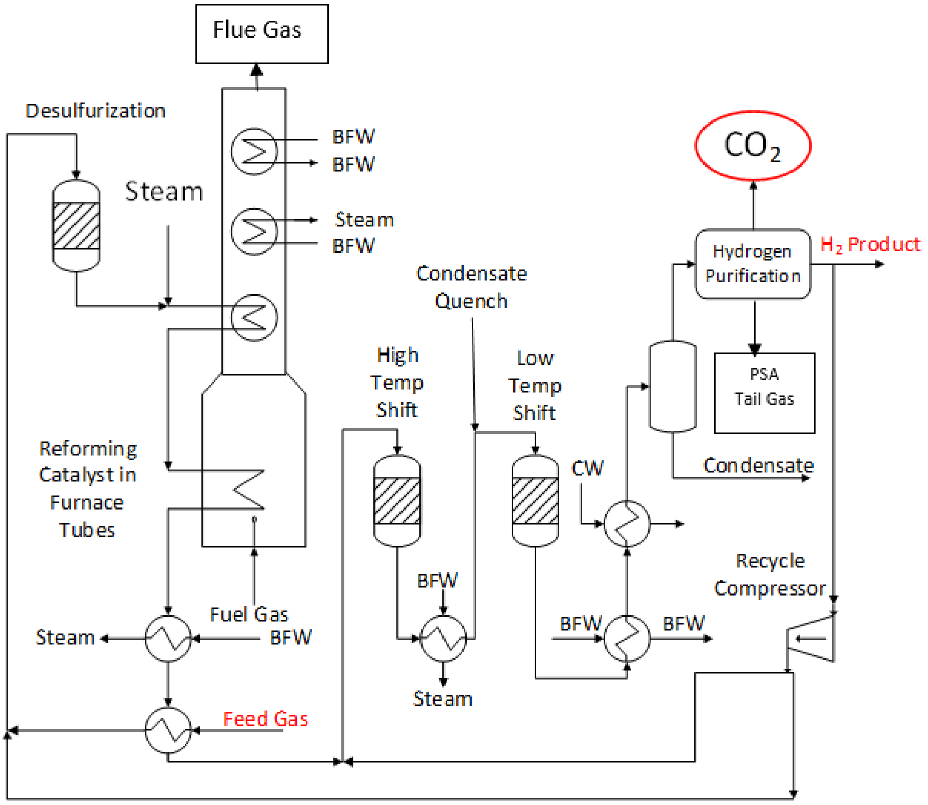


Fig. 11. Process Flow Diagram for a Hydrogen Plant
BFW = Boiler Feed Water; CW = Cooling Water

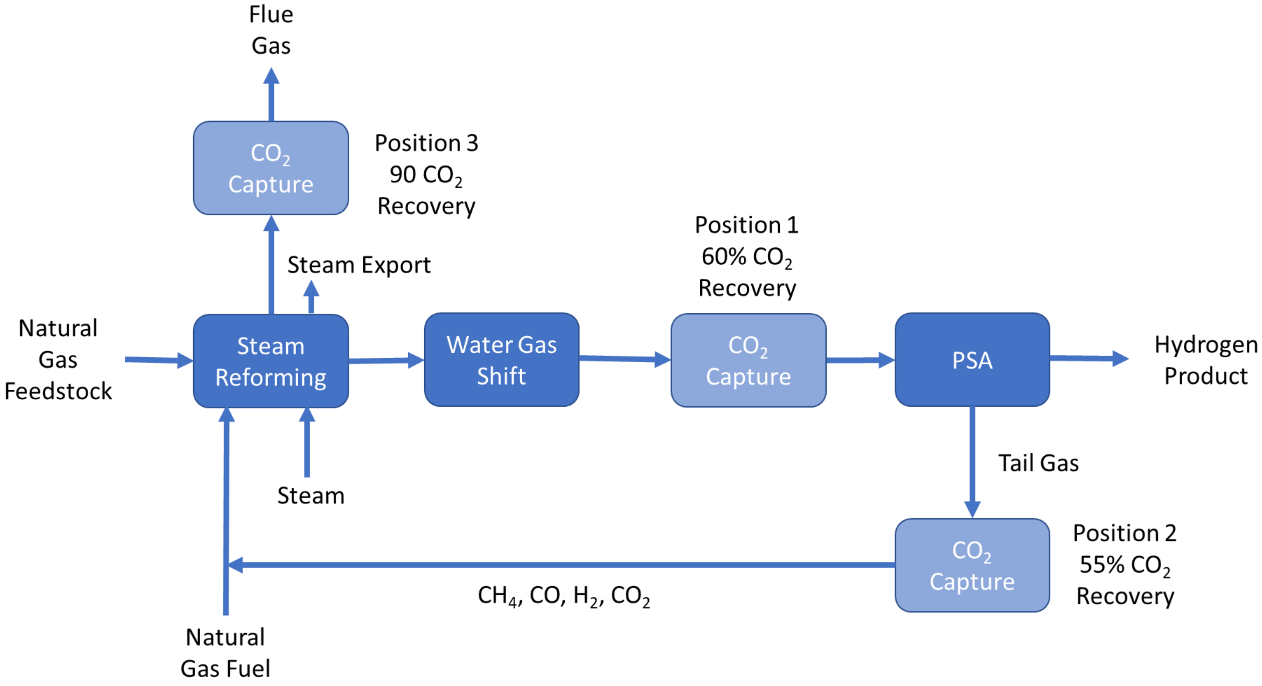


Fig. 12. SRM Hydrogen Plant Block Flow Diagram