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Towards Achieving Net Zero Carbon Dioxide by Sequestering Biomass Carbon

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Abstract— Many corporations aspire to become Net Zero Carbon Dioxide by 2030-2050. This paper examines what it will take. It requires understanding where energy is produced and consumed, the magnitude of CO_2 generation, and the Carbon Cycle. Short reviews are provided for prior technologies for reducing CO_2 emissions from fossil to focus on their limitations and to show that none offer a complete solution. Both biofuels and CO_2 sequestration reduce *future* CO_2 emissions from fossil fuels. They will not remove CO_2 *already* in the atmosphere. Planting trees has been proposed as one solution. Trees are a temporary solution. When they die, they decompose and release their carbon as CO_2 to the atmosphere. The only way to permanently remove CO_2 a*lready* in the atmosphere is to break the Carbon Cycle by growing biomass from atmospheric CO_2 and sequestering biomass carbon. Permanent sequestration of leaves is proposed as a solution. Leaves have a short Carbon Cycle time constant. They renew and decompose every year. Theoretically, sequestrating a fraction of the world's tree leaves can get the world to Net Zero without disturbing the underlying forests. This would be CO_2 capture in its simplest and most natural form. Permanent sequestration may be achieved by redesigning landfills to discourage decomposition. In traditional landfills, waste undergoes several stages of decomposition, including rapid initial aerobic decomposition to CO_2, followed by slow anaerobic decomposition to methane and CO_2. The latter can take hundreds to thousands of years. Understanding landfill chemistry provides clues to disrupting decomposition at each phase.

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

1. Introduction

Carbon dioxide is the dominant greenhouse gas component 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. The most basic statement of a material balance is: In – Out = Net Rate of Accumulation. In order to achieve a net atmospheric accumulation of CO_2 (Net Zero CO_2), CO_2 removal must equal CO_2 production. This paper begins with a short review of some previous proposed solutions. It is not meant to be exhaustive, rather sufficient to show that none are a complete solution to achieve Net Zero CO_2. Permanent sequestration of biomass carbon, in particular tree leaves, is proposed as a simple (in concept), but admittedly daunting (in implementation) method to achieve Net Zero CO_2. This would be CO_2 capture in its simplest, most natural form. It would provide a solution for not only *future* CO_2 from continued use of fossil fuels, but also provide a way to remove CO_2 *already* in the atmosphere and remove it from 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. If one follows trees through their entire life cycle, trees are sustainable. They do pull CO_2 from the air during their life. However, in unmanaged forests, trees lose their leaves every year, which decompose and release their stored carbon back to the atmosphere. At the end of their life, trees die, decompose, and release the carbon stored in their trunks and branches. Trees take care of themselves. However, over their entire life and death cycle, they will not lead to a net reduction in CO_2 that is *already* in the atmosphere.

Biofuels have been proposed to make CO_2 from vehicles renewable. Biofuels do play a role in reducing *future* emissions of CO_2 from the burning of fossil fuels that they displace. However, they come at an economic and societal cost. Almost 40% of the US corn crop is devoted to fuel ethanol production, and almost 30% of US soybean oil is currently going to biodiesel. Biofuels would at best be sustainable [2]. However, they are not, when the fuel required to plant, fertilize, harvest, transport the carbon source, and fuel used in the biofuel processes is considered. Bioethanol from corn will be traced through its Carbon Cycle and will be shown to be both energy inefficient, and an inefficient use of biomass for reducing CO_2. Biofuels from other sources such as cellulosic biomass will be discussed, and a status report will be provided for those technologies.

The technologies for CO_2 sequestration from large industrial furnaces, such as those at power plants will be discussed. The bottom line is: We know how to do it, using modifications of proven technologies that have been used for many years.

However, cost and scaleup will be shown to be issues. CO_2 sequestration can reduce *future* CO_2 going to the atmosphere from continued burning of fossil fuels. It will be a necessary tool in combatting global warming. However, it will not reduce CO_2 *already* in the atmosphere and unsequestered CO_2 from the continued burning of fossil fuels, which will continue to be needed to supply the world's energy demand.

Proper understanding of the Carbon Cycle will show that the only way to reduce the CO_2 *already* in the atmosphere is to grow biomass and remove it from the Carbon Cycle. Some thoughts on how to do this will be presented.

First, it is important to understand the 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 in order to prioritize efforts.

2. The energy scene

The US Energy Information Authority (EIA) provides a database that tracks primary energy production and disposition for the US, and other world regions [3]. BP provides its yearly Statistical Energy Review [4].

Fig. 1 shows the US 2016 primary energy source and sector in which the energy is used [5]. The three largest sources are petroleum (37%), natural gas (29%), and coal (15%). The reality is that in 2016 only about 10% of primary energy came from renewables.

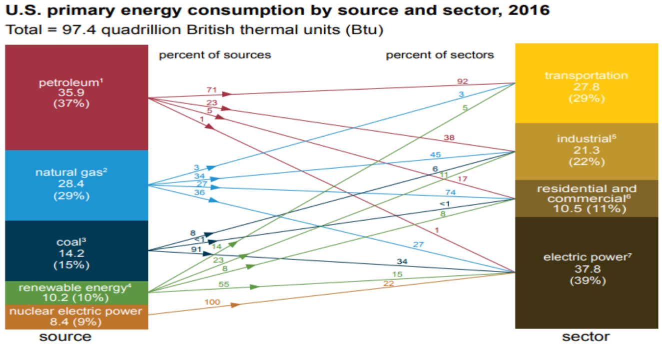

Fig. 1 US Primary energy consumption by source and sector, 2016 Source: EIA (2017) [5]. All rights reserved.

The numbers on the left of the lines connecting sources to 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%. Renewables accounted for only about 10%.

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 going to petrochemicals, 23% 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 giga tonnes (Gt) [5]. 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.

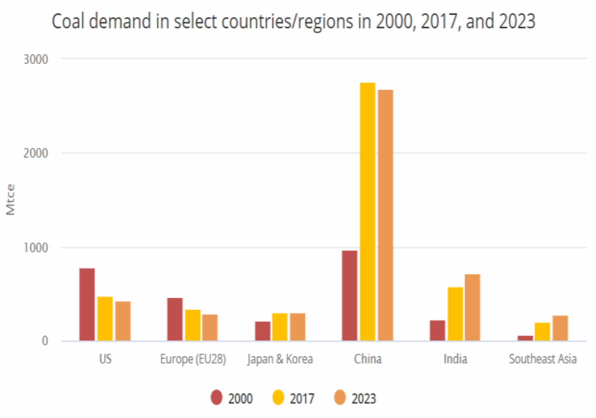

Fig. 2. Coal demand in select countries/regions
Data Source: (EIA, 2017). All Rights Reserved. [5]

The EIA provides a projection for the shift in source of energy for electricity production out to 2050 [6]. Coal and nuclear are expected to decline. Natural gas remains about constant, while electricity from renewable energy is projected to double. The projected shift in source of renewable energy is shown in Fig. 3.

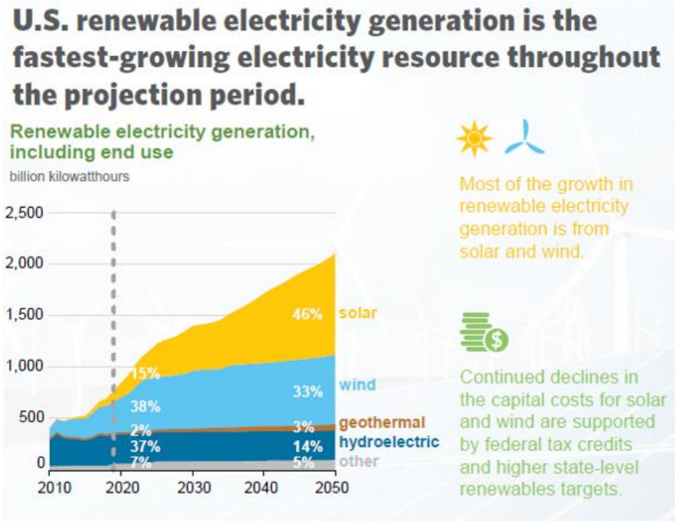

Fig. 3 Shift in source of renewable energy for electricity.

Source: (EIA, 2020). All Rights Reserved. [6]

The absolute amount of electricity from wind is projected to double. Solar is projected to increase by a factor of 9. One question to ask is: 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 at about 36% 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.

Will projections for a great increase in renewables energy come true? R. Malhorta of the Stanford Research Institute (SRI) said the world will need the equivalent energy from 7-9 cubic miles of oil to satisfy the incremental world energy needs to the year 2050 [7]. He argues that renewables cannot provide a complete solution to those needs, stating that *just 1* cubic mile of oil (of 7-9 needed) would require:

- 200 hydroelectric dams the size of the 3 Gorges dam
  (1 every quarter for 50 years);
- 2500 nuclear plants the size of the Diablo Canyon reactor
  (1 per week for 50 years);
- 7700 solar panel parks 10 x the world's largest
  (3 per week for 50 years);
- 3 million windmills
  (1200 per week for 50 years);
- 4.2 billion solar roofs
  (250k roofs per day for 50 years).

Thus, he argues it is impractical to think that petroleum and coal can be displaced completely. That is reality. Energy reduction alone cannot get the world to Net Zero CO_2. In fact, world energy demand will increase with the increase in population, despite energy conservation efforts. Clearly, other solutions are needed.

3. Understanding the Carbon Cycle

A drawing depicting the Carbon Cycle is provided in Fig. 4.

Plants get all of their carbon for their growth from CO_2 in the atmosphere via photosynthesis, forming carbohydrates [9]. The photosynthesis reaction can be represented crudely by the reaction:

$$6\,CO_2 + 6\,H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6\ (\text{glucose}) + 6\,O_2 \quad 1)$$

The simplest formula representation of carbohydrates is CH_2O.

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. Plants and animals that fall to the ground or are buried decompose via the action of worms, fungi, and bacteria. They feed on the decomposing plants, 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%) [10]. 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.

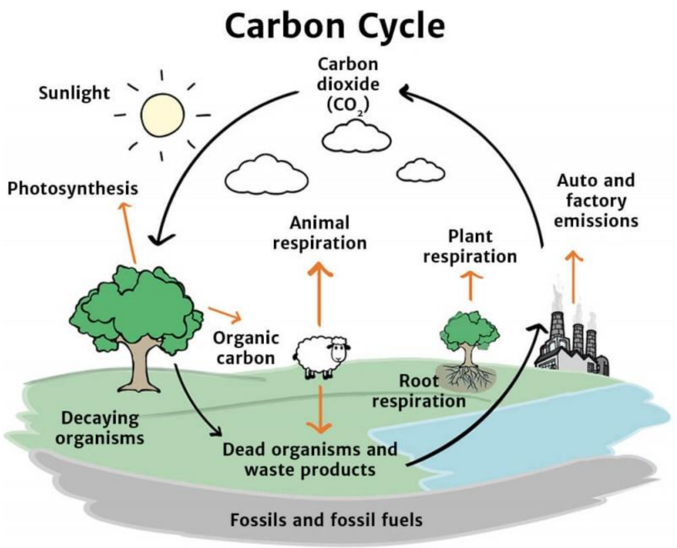

Fig. 4 The Carbon Cycle. Source: Alamy (2020) [8].

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 [11]. In the natural Carbon Cycle, dead plant material returned to the soil feeds the worms, bacteria, and fungi that decompose plant matter releasing the needed N, P, K, and other nutrients back into the soil. That is part of the cycle. Intensive farming requires artificial fertilizer to provide some of the nutrients.

Thus, the normal Carbon Cycle is sustainable. There is no net movement of CO_2 to the atmosphere and no net movement of carbon into the ground. 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).

4. Bioethanol and its Carbon Cycle

The Kyoto Protocol was adopted on December 11, 1997 and entered into force on February 16, 2005 [12]. It called for major industrial countries to reduce emissions of greenhouse gases.

The European response was to shift from gasoline to diesel at the lobbying of the major auto companies. Diesel engines do provide better fuel economy than gasoline vehicles. However, diesel vehicles have issues with emissions of carcinogenic particulates and NOX. We now know that some European car manufacturers cheated on emissions testing, and diesel engines have contributed to health issues [13].

US refineries were configured to make gasoline, with large catalytic reformer and Fluid Catalytic Cracking (FCC) capacity installed in the 1960's and 1970's to make high octane gasoline in response to lead phase out. Thus, the US remained in favor of gasoline. To meet the requirements of the protocol, the US mandated the blending of bioethanol. The US gasoline pool has reached the "blending limit", such that essentially 10% of the US gasoline pool is bioethanol [14]; 10 vol% is the limit for normal gasoline because ethanol is corrosive and degrades elastomers in gaskets of normal gasoline engines. Flex fuel vehicles are now sold that can accept E85 (85% ethanol), but this fuel type is not widely available and has not been widely adopted by the public.

One of the claimed benefits for bioethanol is that the US would become less dependent on foreign oil. With the advent of fracking to release tight oil and gas, and the discovery of oil in the western US, the US has become the largest producer of oil in the world, and now exports about as much finished gasoline and much more oil than the amount of bioethanol blended into gasoline as shown in Fig. 5 [15]-[18]. Thus, the argument that bioethanol is needed for US energy independence no longer holds.

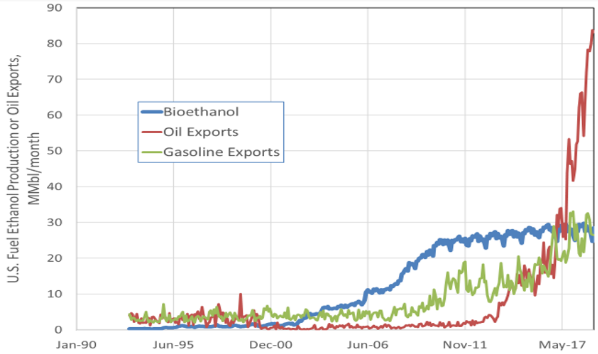

Fig. 5. US bioethanol used in gasoline (blue), oil exports (red), and gasoline exports (green) Data Sources: EIA [15]-[18].

Another early argument for bioethanol was that blending oxygenates into gasoline would reduce tail pipe emissions of carbon monoxide (CO). However, a study in Mexico City showed no indication that CO emissions are reduced with increasing oxygenate concentration for vehicles with 3-way converters [19]. Everything that goes into the converters comes out clean.

In the US, essentially all of bioethanol is made from corn. However, as noted above, transportation is only a fraction of primary energy sector demand, and gasoline is only a fraction of transportation, such that bioethanol represents only about 1.7% of total US energy consumption. Biodiesel penetration is even lower at about 3% of diesel, which is only a fraction of distillates which are lower volume than gasoline in the US [20, 32].

Bioethanol production comes at great economic and social cost and has other issues. The US Department of Agriculture (USDA) indicates that about 40% of the US corn crop is devoted to bioethanol production [21]. That is diverting a lot of potential food into gas tanks. There are other issues. Bioethanol is hygroscopic. It picks up water in pipelines, so it must be blended near gas stations. This adds both capital, labor, and energy costs.

Let me repeat, plants get all of their carbon from CO_2 in the air via photosynthesis. Let us track that carbon through the bioethanol production and Carbon Cycle.

The amount of air with 400 ppmv of CO_2 that it takes to grow an acre of corn is enormous. The calculation is provided in an EXCEL file in the Supplemental Input **SI.1**. It takes the air above about 0.85 acres of land up to the edge of the troposphere (35,000 ft) to feed the growth of one acre of corn. In 2019, 89.7 million acres of corn were planted in the US [21]. The US land area is 2.43E9 acres. Thus, while corn is the largest crop in the US, only about 3.7% of land area in the country is devoted to corn. Of course, not all US land and an even lower fraction of total world land is suitable for growing corn [22]. Thus, it is not reasonable to expect that corn ethanol production can be increased much further.

Corn ethanol is produced by converting starch in corn kernels to sugar and fermenting the sugar to ethanol. Starch is a polymer of the 6-carbon sugars glucose. The sugars are released by hydrolyzing the polymer to break the linkages between the monomers.

A process flow diagram for the current preferred ethanol process, the Dry Grind Ethanol Process is shown in Fig. 6.

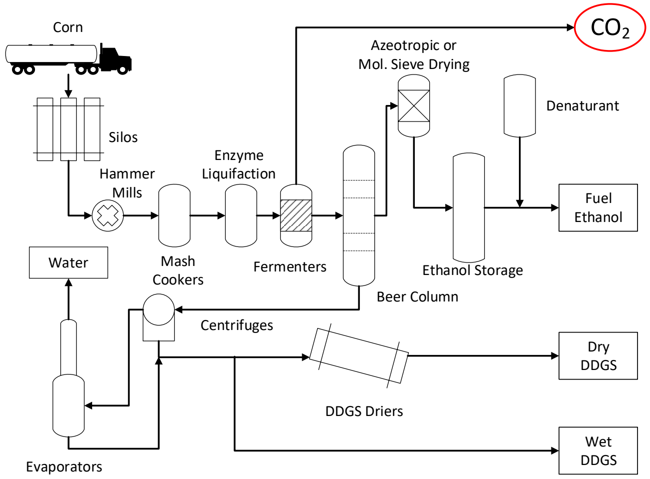

Fig. 6. The Dry Grind Ethanol Process

CO_2 is shown as a product of the Dry Grind Process in Fig. 6. Why?

The simplified molar formula for starch is $C_6H_{10}O_5$, and hydrolysis to glucose can be represented as:

$C_6H_{10}O5 + H_2O \rightarrow C_6H_{12}O_6$ 2)
(1.00 gm starch → 1.11 gm glucose)

The glucose is fermented to ethanol via the reaction:

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$ 3)
1.11 gm → 0.568 gm + 0.542 gm

Thus, fermentation converts two of the six carbons in glucose to CO_2, *before the ethanol does any useful work in a gasoline engine.* CO_2 liberation during fermentation is why champagne is bubbly.

There are over 200 ethanol plants in the US [23]. CO_2 sequestration is possible by absorption or adsorption. However, only a handful recover CO_2. The rest vent to the atmosphere, because recovering CO_2 is expensive, the value of the CO_2 byproduct is low, and most of these plants are in remote regions away from a destination for the CO_2 product. That is reality.

One can already see why corn ethanol is a very inefficient use of carbon in the corn plant biomass to displace fossil fuel carbon. However, corn kernels are only about 60 wt% starch, and the corn plant is only about 35 wt% corn kernels [24]. What happens to the rest of the corn plant carbon as it completes it Carbon Cycle? Most is plowed back into the ground, where it decomposes and releases its carbon as CO_2 back to the atmosphere.

Bioethanol is also very energy intensive. Water and ethanol form an azeotrope. Breaking the azeotrope requires either azeotropic distillation or drying over molecular sieves. Older plants used azeotropic distillation. US Patent Number 4,217,178 discloses a heat integrated ethanol plant with azeotropic distillation [25]. The energy requirement for the distillations is 239.4 kJ/gm mol ethanol. The heat of combustion of ethanol is 1360 kJ/gm mol. Thus, the azeotropic distillation step alone requires 17.8% of the heat of combustion of the product. A full economic model of a Dry Grind ethanol plant, including all utilities costs is provided in Kwiatkowski et al. [26]. The modeled plant uses a molecular sieve drier after distilling the beer to near the azeotrope. That is lower energy than azeotropic distillation. However, with the steam cost converted to the natural gas equivalent, the total plant natural gas equivalent usage is 87% higher than the heat required for the azeotropic distillation step of US 4,217,178. Even though steam for the beer column alone will be less than the azeotropic distillation step, the total plant needs heat elsewhere (cooking the mash, drying the DDGS, etc.). DDGS = Distiller's dried grains with solubles, a byproduct used as animal feed. Thus, bioethanol production is not only an inefficient use of corn biomass carbon, but parasitic energy costs are high. Another issue for corn ethanol in the US is cost. It is not economic without farm subsidies that can amount to over $1 US per gallon [27].

How much CO_2 can be sequestered from US bioethanol production? US nameplate ethanol production is 16,868 MM gal/yr [23]. With 2 mol CO_2 generated per mol of ethanol, sequestering all of the CO_2 would remove 106 MM tons/year CO_2. This is a big number, but only 0.3% of the amount of the 36 Gt/yr CO_2 generated each year worldwide. Thus, other solutions are needed.

What if the US corn plants used to produce ethanol were permanently sequestered? Corn production in the US peaked in the 2017/2018 season at 14,609 MM bushels, with 38.4% going to fuel ethanol. At 35 wt% corn kernels, the weight of corn plants devoted to ethanol was 1.17 Gt [23], [24]. Representing corn as CH_2O, secure burial of those corn plants would have pulled 406.9 MM tonnes/yr of CO_2 from the atmosphere compared to world $CO2_2$ production of 36 Gt/yr or 1.1%. Thus, simply burying the corn plants would be a more efficient means of pulling CO_2 already in the atmosphere, compared to corn ethanol, which is less than sustainable. However, this is nowhere close to what is needed to keep up with the CO_2 entering the atmosphere from the burning of fossil fuels. Thus, the US and the world cannot farm its way out of the CO_2 problem.

The US and Brazil account for about 85% of the world ethanol production. Brazil uses cane sugar as the main raw material, and the energy efficiency of those plants is improved by burning bagasse (waste after squeezing out the cane syrup) to generate power. However, burning bagasse is very dirty and pollution generating, and there is a huge negative environmental impact of clear-cutting forests to grow sugar cane. A better use of bagasse would be permanent sequestration as proposed below to remove that carbon from the Carbon Cycle. Instead of clear cutting and burning trees, which releases CO_2 to the atmosphere, a better solution would be secure sequestration to permanently remove that biomass from the Carbon Cycle.

5. Cellulosic ethanol

Cellulosic ethanol has been touted as the Holy Grail for bioethanol. Advantages would be cheap, non-food feedstock. However, its implementation has been slow. A Sandia study indicated that 70 billion gallons of cellulosic ethanol should be "possible" by 2030 [28]. However, only about 15 MM gal were produced in 2018 [29]. The reality is that continued economic and technical challenges remain.

A dated study estimated capital and production costs for a cellulosic ethanol plant showed the net back price for cellulosic ethanol was 3.2 times the then current sales price of corn ethanol [30]. The cost challenge as of 2011 was:

Current Ethanol Sales Price:	$2.15
Ethanol Yield	79 gal/ton (76% efficiency)
Ethanol Production Volume	61.0 MM gal/yr
Capital Investment	$423 million
TCI per annual gal	$6.92

Cellulose is a polymer of sugars that has a different structure than starch as shown in Fig. 7.

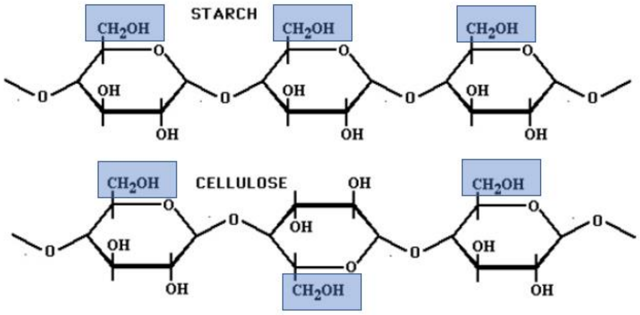

Fig. 7 The difference between starch and cellulose

In starch, the CH_2OH groups of the monomers are on the same side of 6-member ring. In cellulose, they are on the opposite side of the rings. This leads to cross linkage, which leads to dense packing of the polymer chains as shown in Fig. 8, making cellulose insoluble in water, and attack by enzymes to hydrolyze and unzip the polymers and release the sugar monomers slow. Special, high cost enzymes are needed. Cellulose also incorporates pentose monomers in addition to glucose monomers. A cellulose pretreatment step is required ahead of fermentation. Pretreatment may involve treatment with strong or dilute acids, ammonia, or alkaline peroxides. Thus, the pretreatment step may be corrosive, requiring high cost materials of construction, such as stainless steel, instead of low-cost carbon steel. The chemicals used in the pretreatment step may convert the pentose monomers to furans, which may inhibit enzyme attack, further slowing the kinetics. Slow kinetics means large pretreatment vessels, further increasing the cost of the pretreatment step. Thus, the pretreatment step may add one third to the capital cost ahead of fermentation which currently makes cellulosic ethanol less economic than corn ethanol, which already struggles economically.

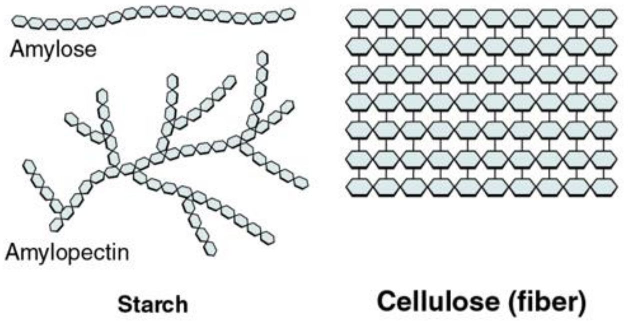

Fig. 8 The difference in packing structure between starch and cellulose.

Plant biomass also includes lignin in addition to cellulose, which becomes a byproduct and lowers ethanol yield based on total biomass carbons. Byproduct lignin yield is high, and lignin becomes a nuisance byproduct. (Note the estimated low 76% yield above). Lignin is a polymer of alkyl aromatics and polynuclear aromatics. It cannot undergo normal aerobic or anaerobic decomposition.

Thus, while cellulose may be a cheaper feedstock than corn, total cost of production must be considered, including capital charge and operating costs. The higher cost of capital, lower yield, and lignin formation currently outweigh the cheaper feedstock cost.

Instead of spending money on capital, high-cost enzymes, and other operating costs to convert cellulose to ethanol, sequestration of the cellulosic biomass, as proposed below, may be a more effective way to remove that biomass carbon from the Carbon Cycle.

6. Biodiesel

Biodiesel is produced by the transesterification of vegetable oils with methanol. The reaction is shown in Fig. 9.

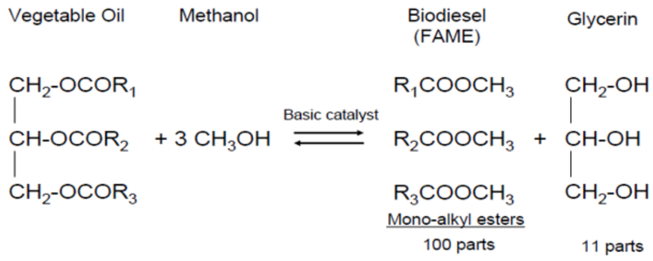

Fig. 9. Transesterification of vegetable oils to produce biodiesel (FAME) and glycerin as a byproduct.

Economic production of methanol requires large plants to achieve economy of scale, and the ethanol is made from cheap natural gas from fracking [31]. Thus, the methanol comes from a fossil fuel. The reaction makes fatty acid methyl esters (FAME) having carbon numbers in the diesel boiling range. FAME has cetane and other properties that make it acceptable for blending into diesel. It cannot used neat for various reasons, and thus, the diesel pool will continue to rely on diesel from fossil fuels.

One of the biggest issues for biodiesel is the production of about 11 parts glycerin, a nuisance byproduct, per 100 parts FAME.

Rather than spending capital and energy converting biomass to biofuels, simply burning the biomass as a renewable energy source to produce power may be a more cost-effective solution. Indeed, this is being commercialized now on a large scale. However, there are issues (low heat content, soot formation, etc.)

7. CO_2 Sequestration Technologies

CO_2 sequestration can remove CO_2 from industrial furnaces, including furnaces used in the generation of electricity from coal or natural gas. Thus, it can target *future* CO_2 generation from the industrial and electric power sectors, which together account for over 50% of CO_2 generation. This is substantial, but not a complete solution to the CO_2 problem.

The message for CO_2 sequestration is: We know how to do it, with proven technologies, some of which have been practiced for close to 100 years. It is going to cost money, and scale-up to the size needed is going to be an issue.

Three ways have been proposed for CO_2 sequestration; high-level bullet points for some of the advantages and disadvantages are provide below and will be discussed in more detail.

Direct CO_2 Capture from air

- Dilute (400 ppmv CO_2);
- Must move *massive* quantities of air;
- Can remove CO_2 *already* in the air.

Post-Combustion CO_2 Capture

- Fuel burned and CO_2 removed from furnace stack gas;
- CO_2 still dilute (5-10 vol% depending on fuel source and composition) due to nitrogen from combustion air;
- Flue gas near atmospheric pressure, and must be blown (compressed) through absorber or adsorption bed;
- Can be applied to flue gas from natural gas or coal-fired power plants making both “clean,” i.e. CO_2 free;
- Appropriate to sequester CO_2 from massive *existing* furnace installed base.

Pre-Combustion CO_2 Capture

- Requires new-build integrated combined cycle power plants.

- For natural gas fuel, basically modification of a steam reforming H_2 plant which has been practiced for nearly 100 years.
- Steam reforming of natural gas or partial oxidation of coal to form syn gas ($CO + H_2$).
- Water-gas shift to produce CO_2 and more H_2: $CO + H_2O = CO_2 + H_2$ 4)
- CO_2 removed by absorption or adsorption, before producing a clean burning H_2 fuel (pre-combustion);
- In a combined cycle power plant, exothermic reactions produce steam to turn turbines to generate electricity,
- Hydrogen can be burned to generate more steam to make more electricity or exported for refinery or chemical use or other fuel use.
- The so-called “Hydrogen Economy”.

All CO_2 sequestration technologies will face the issue of what to do with the CO_2 product, especially at the scale needed to keep up with the new introduction of CO_2 into the atmosphere from continued use of fossil fuels (currently 36 Gt/yr).

7.1 *Direct CO_2 capture from air*

There are companies trying to commercialize pulling CO_2 directly from air [33]. The obvious issue is the need to move *massive* quantities of air through an absorber or adsorber to recover even a trivial amount of CO_2. In my opinion, this is simply not practical. (See the amount of air needed to supply CO_2 to grow just one acre of corn above).

7.2 *Post-combustion CO_2 capture*

A process schematic for post-combustion CO_2 capture is shown in Fig. 10.

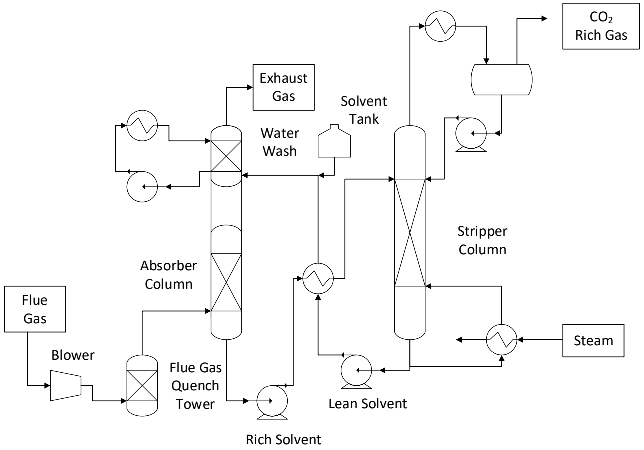

Fig. 10 The post-combustion CO_2 capture process

The heart of the process is adsorption into a solvent, typically an amine, followed by stripping the CO_2 from the amine via distillation. Typical solvents include MEA (monoethylamine) and DEA (diethylamine), which requires less energy to strip the amine than MEA.

This technology can be retrofitted on the massive installed base of existing furnaces of power plants, and refinery and chemical processes. Thus, it should be an essential part of a comprehensive attack on global warming from CO_2.

In Post-Combustion capture, flue gas is near atmospheric pressure and must be blown through an absorber or adsorption bed. This requires a blower (low pressure compressor) and its associated capital and operating cost. One issue for post-combustion CO_2 capture is that the CO_2 is still dilute due to nitrogen from the air used to combust the fuel. The technology can be retrofitted to either natural gas- or coal-fired power plants. The concentration of CO_2 in the flue gas can be calculated from the composition of the fuel. For methane combustion, the reaction is:

$CH4 + 2\ O_2 + 2*79/21\ N_2 \rightarrow CO_2 + 2\ H_2O + 2*79/21\ N_2$ 5)

Since combustion air is 79 mol% N_2, it dilutes the CO_2 product. Also, furnaces are operated with a small amount of excess air.

CO_2 concentration would vary from about 5 mol% for natural gas to 10 mol% for coal due to its higher C:H ratio, which depends on the grade of coal.

The flue gas from the furnaces is hot. Absorption is endothermic, and thus is favored by lower temperature. The flue gas must first be cooled in a cooling or quench tower. This tower also knocks out some of the water of combustion down to its vapor pressure at the temperature at which this tower operates. A water pump around may be used as shown. The absorber itself must be cooled by cooling water. The absorber would typically have two sections as shown: a lower section where a rich amine solution is sent to the top of the section and this section acts as a true stripper. The upper section would include a water pump around with further cooling to reduce the concentration of amine in the product gas stripped of CO_2.

The rich amine solution (rich in CO_2 but diluted by remaining water from combustion) exits the bottom of the tower and is pumped through a preheat feed/effluent exchanger to the CO_2 stripping tower. CO_2 product is taken overhead, compressed to liquify, and sent to storage. The lean amine solution stripped of CO_2 is recycled back to the absorber.

The air to large industrial furnaces is controlled by dampers. Large furnaces typically run at 2-4% excess oxygen (and of course 79/21 times more nitrogen). Oxygen can degrade the amine absorbent or solid adsorbent, an issue not seen in steam reforming of methane without added oxygen, which may require absorbent clean up and makeup. Solid adsorbents are being investigated as an alternative to absorption to save energy from the amine stripping step. This technology works and removal of acid gases like CO_2 and H_2S from refinery streams has been practiced for about 100 years. Application to recover CO_2 from power plant flue gas is in the demonstration stage. A demonstration plant was built by Alabama Power [34], [35]. That demo unit pulls CO_2 from the flue gas of the equivalent of 25 MW of power generation. The plant occupies a plot space of 90 m X 45 m. A large power plant may be 1000 MW, and thus, a CO_2 capture plant to treat the entire power plant effluent will be massive. This shows the issue with scale up. Production of amine is energy intensive, and a massive amount of amine would be needed to treat significant amounts of flue gas.

The technology has now been scaled up to semi-commercial scale. The Petra Nova power plant began commercial sequestration from flue gas of the equivalent of 240 MW (37% of the total plant emissions) in January 2017 [36], [37]. It is a start, but there is a long way to go. That is the reality.

7.3 *Pre-combustion CO_2 capture*

Pre-Combustion CO_2 capture involves steam reforming or partial combustion of a fuel to form synthesis gas (a mixture of CO and H_2). In principal, any fuel containing carbon can be converted to synthesis gas.

For high H:C fuels, CO is converted by reacting with water to form CO_2 and more H_2 via the water gas shift reaction.

Steam reforming is preferred for natural gas. The reaction for methane is:

$CH_4 + H_2O = CO + 3\ H_2$ 6)

For coal, partial oxidation is preferred:

$C + ½\ O_2 \rightarrow CO$ 7)

The steam reforming reaction forms some hydrogen directly.

Both steam reforming and partial oxidation reactions are followed by the water-gas shift reaction to form more hydrogen and CO_2:

$CO + H_2O = CO_2 + H_2$ 8)

The CO_2 is captured by absorption or adsorption. One advantage for pre-combustion capture compared to post-combustion is that the water-gas shift reactor effluent is at moderate pressure (10-20 barg). Thus, it does not need a separate blower to move it through an absorber or adsorber, and adsorption processes that use pressure swing are possible.

Steam reforming of methane is the technology used in hydrogen plants, a technology that has been used for nearly 100 years to produce supplemental hydrogen for refineries and chemical processes.

A schematic of a steam reforming hydrogen plant is provided in Fig. 11.

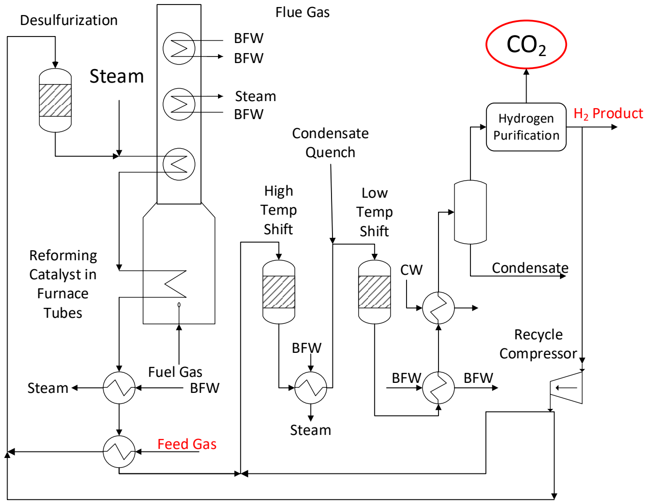

Fig. 11. Process Flow Diagram for a Hydrogen Plant BFW = Boiler Feed Water; CW = Cooling Water

Feed gas is preheated and pretreated to remove sulfur. For natural gas with low levels of sulfur, this may be removed by passage through a bed of zinc oxide where the sulfur is converted to zinc sulfate. Feed gases with higher amounts of sulfur (coal, for example) require a hydrotreater.

The pretreated gas is mixed with steam (and some recycled hydrogen product) and reformed over a catalyst at high temperature. For typical smaller size 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 is usually 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 favor higher equilibrium conversion.

CO_2 is removed from the shift reactors effluent by either absorption in an amine solution, followed by stripping of the CO_2 product by distillation, which requires steam, or by adsorption on a molecular sieve bed followed by desorption by pressure swing or temperature swing.

The hydrogen atoms in the methane are converted to water. The water is manly removed by cooling and separation in a condensate drum. CO_2 is separated in the hydrogen purification section, by absorption or by adsorption in a Pressure Swing Adsorption (PSA) unit, as shown in Fig. 10.

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. CO_2 is removed from the water-gas shift reactor effluent, compressed to liquify, and sent to storage. Thus, a clean high purity hydrogen product is produced. In a combined cycle power plant, the hydrogen (the Pre-Combustion fuel 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).

Partial oxidation of coal or other high carbon content fuels is usually done in open flame reactors, preferably using pure oxygen, because air would dilute the synthesis gas by the nitrogen. Thus, for coal, the Oxy-Fuel Pre-Combustion process shown in Fig. 12 may be preferred [38].

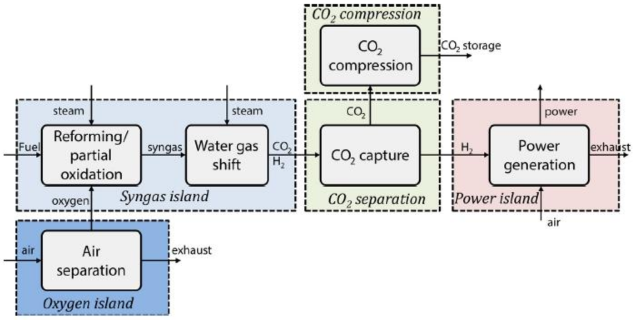

Fig. 12 Oxy-Fuel Pre-Combustion Combined Cycle Power Plant. Source: Jansen et al. [38]

One obvious drawback is the need for an air separation plant to generate the pure oxygen. One can envision an Oxy-Fuel Pre-Combustion plant, where the nitrogen from the air separation plant is used with the hydrogen product to produce ammonia.

8. Sequestration of biomass *carbon*

As noted earlier, fossil fuels and CO_2 sequestration will prevent *future* CO_2 from fossil fuels entering the atmosphere. However, doing it on a scale needed to meet current and future energy demands is daunting. Furthermore, CO_2 sequestration is not a complete solution, so other solutions are needed.

Per an understanding of the Carbon Cycle, the only way to remove CO_2 *already* in the atmosphere is to grow biomass and remove that biomass from the Carbon Cycle. We have already argued that growing corn and sequestering the total corn plant mass would have a bigger impact than inefficiently converting only a portion of that biomass (starch in corn kernels) to fossil fuels. That would pull some CO_2 *already* in the atmosphere. However, as shown above it is not enough. Sequestering all of the biomass in the 40% of the US corn crop now devoted to bioethanol would only remove 406.9 MM metric tonnes of CO_2 per year compared to the 36 Gt generated. Something else is needed to achieve Net Zero CO_2 to the atmosphere.

The answer is secure burial of biomass from other sources, including municipal and yard waste and biomass generated in forests (tree leaves and wood). Secure burial means permanent burial with provisions taken to prevent decomposition and release of the CO_2 to the atmosphere. Some thoughts on how to achieve secure sequestration with minimal or no CO_2 to the atmosphere are provided in the next section.

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. In addition, it would remove CO_2 going to the atmosphere from refinery and petrochemical processes used to produce plastics, if plastics are included in the waste to be buried. The systems are in place to collect yard and municipal waste in most large cities in the US, and elsewhere in the world, so part of the cost is already sunk.

Most municipal yard waste is buried in landfills [39]. Some municipal waste is now burned to generate renewable power [40]. 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. 13, that must be separated before the organics can be burned [41]. Secure burial 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 [41]. In 2017, the total amount of US municipal and yard waste generated was 267.8 MM tons. Some is separated and recycled, some is currently burned to generate renewable power, leaving the amount landfilled at 139.6 MM tons, with composition provided in Fig. 13. The organic component was 112.5 MM tons. That corresponds to 149.6 MM metric tonnes of CO_2 if allowed to completely decompose. This compares to the 6480 MM tons 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 resources are needed for pulling CO_2 from the atmosphere: trees, both tree leaves and/or wood. The USDA has provided allometric equations for urban tree growth parameters for many species and at numerous locations in the US [42]. The growth equations have been programmed into EXCEL files which are available in **SI.2**. Dry leaf biomass is calculated for most species and regions where data are available.

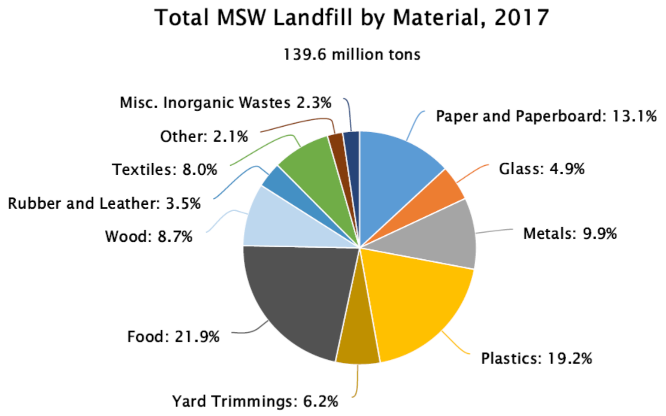

Fig. 13. US 2017 Municipal and Yard Waste Landfilled Source: (EPA, 2020) [41].

Dry leaf biomass for some species of maple trees at various locations in the US are shown in in Fig. 14, as an example. Data for other tree species are provided in **SI.2**. 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 wgt)*(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 [43], [44]. 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 CO_2, compared to 36 Gt 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 is still daunting.

Mature tree wood weights can be several metric tonnes per tree, as shown in Fig. 15. 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 the 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 bagasse should be considered instead of burning it to produce power, which releases the bagasse CO_2 back to the atmosphere, albeit renewable CO_2. 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.

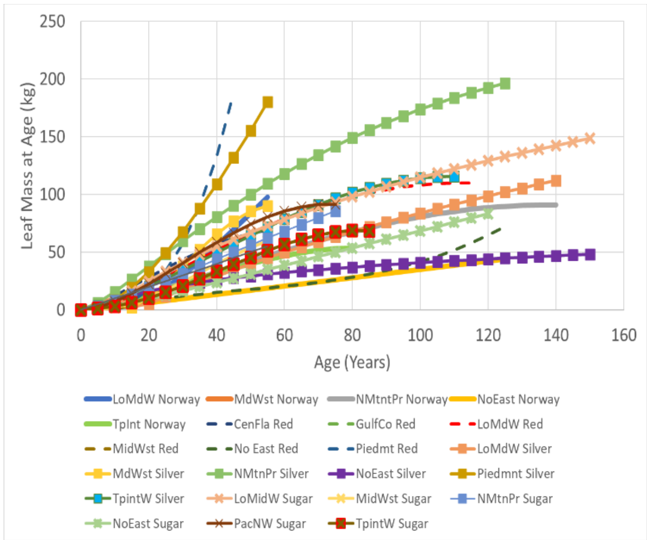

Fig. 14. Yearly dry deaf biomass generation by some maple tree species in various regions of the US
Source: McPherson, van Doorn, and Peper (2016) [42].
The US regions include: LoNdWst=Lower Midwest; MidWst=Midwest; NMtnPr=North: No East = North East; CenFla=Central Florida; GulfCo=Gulf Coast; Piedmt=South.

Figures 14 and 15 represent calculations from the regression equations for the allometric tree growth equations provided by McPherson, van Doorn, and Peper (2016) [42]. 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.

Figure 16 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 exceeds 50% to over 70% of the total biomass generated over the life of the tree.

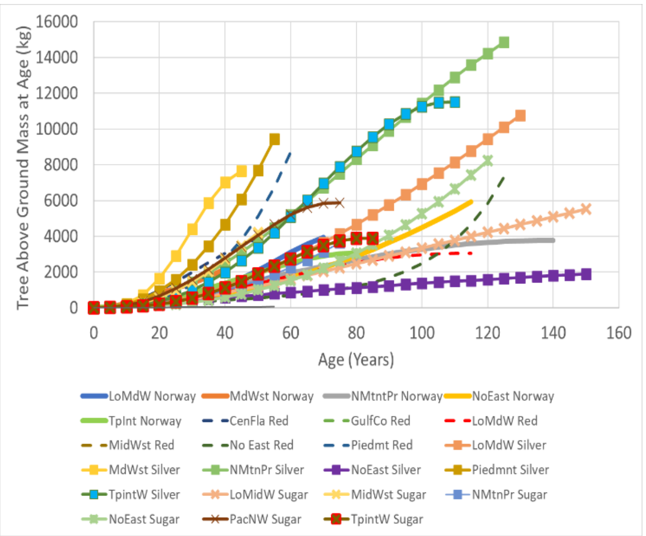

Fig. 15. Above ground biomass for some Maple tree species in various regions of the US.
Source: McPherson, van Doorn, and Peper (2016) [42].

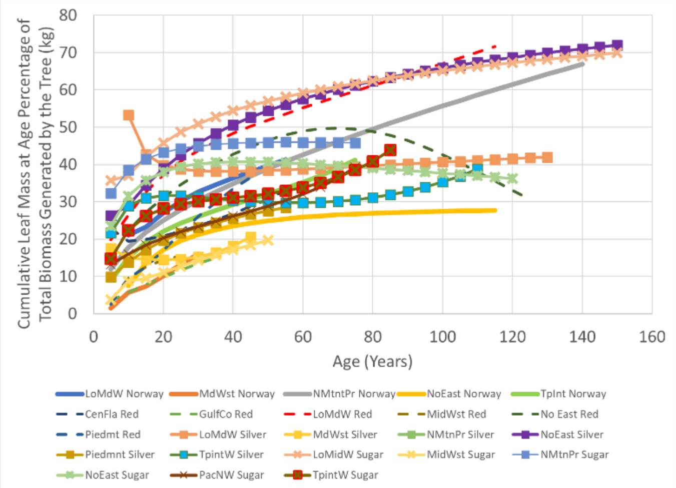

Fig. 16. Calculated cumulative leaf biomass as a percentage of total biomass generated over the life of various species of Maple trees at various locations in the US.

9. 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 to minimize volume. Permanent sequestration requires discouraging waste degradation in landfills.

Some municipal waste is now burned to generate renewable power [40]. One issue for that application is that even after separation of recyclables, average municipal waste still contains about 20% non-organics (glass, metal, etc.) that must be separated before the organics can be burned [41]. Secure burial to sequester all of the waste would not require this stringent and costly separation.

Municipal waste is buried in landfills, where it slowly decomposes. It undergoes a combination of aerobic and anaerobic decomposition to produce a biogas. Modern landfills undergo several distinct stages [39], [45]-[47].

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.

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.

Phase III (Methane Formation)

Phase III decomposition starts when certain kinds of 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 symbiotic, or 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, 40% to 60% carbon dioxide.

Phase V (Mature Phase)

Landfills may 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, e.g. as bioavailable phosphorus becomes increasingly scarce. CH_4 production almost completely disappears. Thus, complete decomposition may take hundreds to thousands or even millions of years.

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 is a more powerful greenhouse gas 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.

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.

Simplified equations for anaerobic degradation of cellulose are:

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

Hydrolysis (depolymerization) of cellulose to release sugars.

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

Anaerobic digestion to form methane and CO_2.

Water is needed to first depolymerize the 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 leaves 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 [48]. 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. The model for it is the story of how coal and oil were formed. 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.

10. Are Steps to Prevent Degradation in a Landfill Absolutely Necessary?

Steps to reduce or eliminate biomass degradation are desirable but will add cost. Are they absolutely necessary?

Coscuner, et al. [49] modeled landfill gas generation in a landfill in Bahrain.using the US Environmental Protection Agency's Landfill Gas Emission Model software [50]. 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 after 120 years following landfill closure. That landfill opened in 1987 and closed in 2019. The total amount of waste deposited was 23,172,413 Mg. The MSW (Municipal Solid Waste) was comprised of The model requires input of DOC=Degradable Organic Carbon.

$$\mathrm{DOC} = 0.4\,(A) + 0.17\,(B) + 0.15\,(C) + 0.3\,(D) \qquad 11)$$

where A is the fraction of 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. Note that 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 PTA, or polyolefins do not contain oxygen atoms.

The EPA model predicts an exponential decline in biogas generation (methane and CO_2) for 120 years after landfill closure. Figure 17 shows that if the model were extrapolated to 500 years, the percentage of decomposable material that would have decomposed reaches an asymptote of about 18%. The calculations are provided in **SI.3**. Thus, if one were to take no additional action to prevent biomass degradation, over 80% of the decomposable biomass would never decompose, thus proving the premise of this manuscript that secure landfilling of biomass is a viable way to pull CO_2 from the atmosphere to offset CO_2 from continued use of fossil fuels.

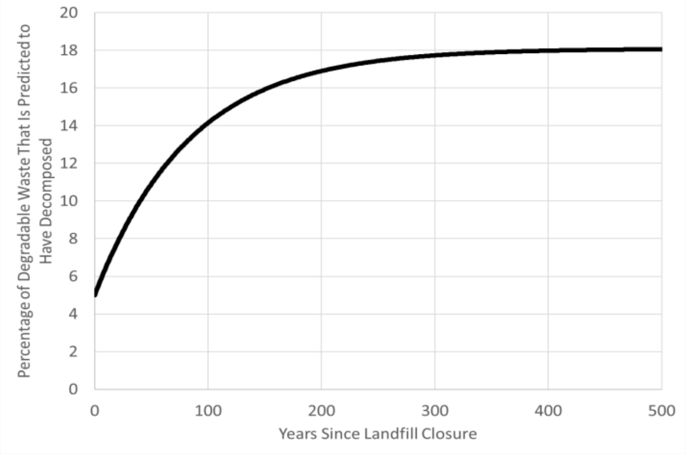

Figure 17. Percentage of degradable biomass that would decompose calculated by extrapolating the US EPA Landfill Gas Emissions Model (LandGEM) for a landfill in Bahrain [49], [50].

11. Final Comments

Here are some final comments regarding the proposal of permanent biomass sequestration as a means of removing CO_2 already in the atmosphere as a move towards achieving Net Zero CO_2.

- Theoretically can it achieve Net Zero CO_2? Yes, and on its own independent of other technologies.
- Is it technically sound? Yes. It is thought that landfills can be designed to prevent biomass degradation to CO_2 and/or methane. In fact, encouraging degradation may be a more difficult problem as evidenced by the huge mounds left by traditional landfills. Geologic formations that are currently being considered for CO_2 sequestration should also be considered.
- Is it actionable? Yes. It is believed it could be put into practice in the timeframe required (before 2035-2050).
- Are there secondary issues? Yes: 1) Designing new managed forests with leaf collection in mind; 2) Soil nutrient replacement, etc.; and 3) Designing secure leaf landfills with no or minimal decomposition and leakage. However, it is thought that these issues can be addressed by gathering the right group of people (experts in forestry, soil chemistry, landfill management).
- 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 the move to renewable energy, CO_2 sequestration, etc. Even at incomplete implementation, it can play a role in reducing net CO_2 to the atmosphere.
- Can any of the other proposed technologies achieve Net Zero CO_2 on their own? No.
- How would biomass landfill projects be funded? Carbon credits are currently being traded. The business model for this proposal would be: Corporations would invest in the landfills, and sell carbon credits to recover their investment.

12. Conclusions

Carbon dioxide from fossil fuels is the main culprit of Global Warming. The problem is massive; 36 Gt/yr CO_2 are being released into the atmosphere. Finding a solution requires an understanding of where energy is produced and consumed and a proper understanding of the Carbon Cycle. While renewable energy is growing rapidly, it remains a very small part of overall energy. Other solutions are needed.

Bioethanol and biodiesel remain a small part of energy for transportation, which itself is less than 30% of overall energy consumed. Corn ethanol is traced through its Carbon Cycle. Biofuels would at best be sustainable, but are not, when energy for their production, and the stoichiometry of the fermentation reaction are considered. Two of the six carbons of glucose are converted to CO_2 during fermentation, which most facilities release to the atmosphere before any useful work is done in an engine. Cellulosic ethanol promises cheap feedstock, but still faces a number of technical and economic challenges. This has slowed implementation. The reality is that only about 15 MM gallons of cellulosic were produced in 2018 compared to 16,868 MM gal of corn ethanol.

CO_2 sequestration targets CO_2 produced in large industrial furnaces, including those used to generate electric power. Industrial and power plant furnaces account for about half of CO_2 generated. This is significant, but CO_2 sequestration will not be a complete solution. The message is: We know how to do it, using variations of technologies that have been used for over 100 years. It is just going to cost money and scaleup is a major issue. Post-combustion capture can be retrofitted to the massive installed base of industrial furnaces, and thus, must be an essential part of solving the CO_2 problem. Pre-combustion capture is a variation of a hydrogen plant, which produces a clean burning hydrogen product that can be burned in a combined cycle power plant to generate more electricity or exported for use in a refinery, chemical plant, or even for residential use (a hydrogen economy). Natural gas can be steam reformed, and coal can undergo partial oxidation. With CO_2 sequestration, both natural gas and coal can become CO_2-free fuels. To date, few commercial-scale sequestration projects have been brought forward. What to do with all of the sequestered CO_2 remains a challenging problem

Biofuels and carbon dioxide sequestration can displace *future* CO_2 from continued use of fossil fuels. The only way to reduce CO_2 *already* in the atmosphere is to grow biomass from atmospheric CO_2 via photosynthesis and permanently sequester that biomass. Rather than spending capital and energy to convert that biomass to biofuels, which is both energy inefficient and an inefficient use of biomass carbon, permanent sequestration of biomass *carbon* from tree leaves, crops, and municipal and yard waste is proposed. Theoretically, sequestration of only a fraction of the world's tree leaves can bring the world to Net Zero CO_2 and without disruption of the underlying forests. Thoughts are put forth on how to redesign landfills to achieve secure permanent biomass sequestration.

ACKNOWLEDGMENT

Amelse received a Ph.D in Chemical Engineering from Northwestern University, Evanston, IL USA. He worked for Amoco Chemical Company R&D (now 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 collaborating with Dr. Luis Mafra on the characterization of molecular sieve catalysts and adsorbents via Solid State NMR, work started while he was 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 U.S. This article was developed as an independent contribution between assignments at the university. As such, he declares no organizational funding for this article.

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