



## RENEWABLE DIESEL AS A HEATING FUEL OPTION FOR NEW YORK CITY BUILDINGS

**INFORMATIONAL REPORT** 

#### **ABSTRACT**

This study evaluates the potential for using renewable diesel (RD) fuel and its blends as options for heating municipal buildings in New York City. This report presents relevant information regarding New York City's concerns with global warming and greenhouse gas emissions. In addition, this report provides a technical overview of renewable diesel (RD), which includes details on existing and probable production sources, and current uses of renewable diesel (RD) worldwide and in the United States. By implementing this first-of-its kind strategy, the City of New York would spearhead the use of renewable diesel (RD) and its blends as heating fuels for buildings in the United states and throughout the world.



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#### **ABSTRACT**

This study evaluates the potential for using renewable diesel (RD) fuel and its blends as options for heating municipal buildings in New York City. This report presents relevant information regarding New York City's concerns with global warming and greenhouse gas emissions. In addition, this report provides a technical overview of renewable diesel (RD), which includes details on existing and probable production sources, and current uses of renewable diesel (RD) worldwide and in the United States. By implementing this first-of-its kind strategy, the City of New York would spearhead the use of renewable diesel (RD) and its blends as heating fuels for buildings in the United states and throughout the world.

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#### **ABBREVIATIONS AND ACRONYMS**

ABBREVIATIONS/ACRONYMS	DEFINITIONS	
AQI	Air Quality Index	
ASTM	American Society of Testing and Materials	
CARB	California Air Resources Board	
CDC	U.S. Centers for Disease Control and Prevention	
CFC	Chlorofluorocarbon	
CH4	Methane	
СО	Carbon Monoxide	
CO2	Carbon dioxide	
CO2e	Carbon Dioxide Equivalent	
COPD	Chronic Obstructive Pulmonary Disease	
DCAS	New York City Department of Citywide Administrative Services	
DOE	Department of Energy	
EIA	Energy Information Administration	
EPA	U.S. Environmental Protection Agency	
EPICA	European Project for Ice Coring in Antarctica	
FAME	Fatty Acid Methyl Esters	
FTD	Fischer-Tropsch Diesel	
gCO2e/MJ	Grams of Carbon Dioxide Equivalent per Megajoule of Energy	
GHG	Greenhouse Gas	
GTL	Biogas-to-liquids	
GWP	Global Warming Potential	
HC	Hydrocarbon	
HCFC	Hydrochlorofluorocarbon	
HDRD	Hydrogenation Derived Renewable Diesel	
HFCs	Hydrofluorocarbons	
HHS	Department of Health and Human Services	
HVO	Hydrogenated Vegetable Oil	
IPCC	Intergovernmental Panel on Climate Change	
IRS	Internal Revenue Service	
IRS	Internal Revenue Service	
MtCO2e	Metric Tons of Carbon Dioxide Equivalent	
N2O	Nitrous Oxide	
NASA	U.S. National Aeronautics and Space Administration	
NF3	Nitrogen Trifluoride	
NO	Nitric Oxide	
NO2	Nitrogen Dioxide	
NOAA	National Oceanic and Atmospheric Administration	
NOx	Nitrogen Oxides	
02	Oxygen	
03	Ozone	
PFCs	Perfluorocarbons	
PM	Particulate Matter	
pMC	Percent Modern Carbon	



#### **ABBREVIATION AND ACRONYMS (continued)**

ABBREVIATIONS/ACRONYMS	DEFINITIONS	
ppb	Parts Per Billion	
ppm	Parts Per Million	
RD	Renewable Diesel	
REG	Renewable Energy Group	
SF6	Sulfur Hexafluoride	
TC	Total Carbon	
tCO2e	Metric Tons of Carbon Dioxide Equivalent	
THC	Total Hydrocarbons	
TOC	Total Organic Carbon	
UCO	Used Cooking Oil	
ULSD	Ultra-low Sulfur Diesel	
USDA	U.S. Department of Agriculture	
USGCRP	U.S. Global Change Research Program	
UV	Ultra Violet	
VOCs	Volatile Compounds	



#### **EXECUTIVE SUMMARY**

The City of New York recognizes the reality of climate change and the catastrophic effects of global warming. Further, the City is conscientious of the fact that reducing greenhouse emissions that cause the unprecedented warming of the earth is of utmost importance in mitigating the detrimental effects of climate change that are being experienced around the globe.

For these reasons, in September 2014, the City of New York made a public commitment with its *One City Built to Last* plan <sup>1</sup> to reduce the City's greenhouse gas emissions 80 percent below the 2005 levels by 2050 (80 X 50), this way positioning the City on a path to become the most sustainable big city in the United States and a front-runner in the task of achieving a better global environment.

In 2015, the City published *One New York, The plan for a Strong and Just City,* which is a comprehensive plan that solidifies New York City's commitment towards attaining two critical goals:

- 1. New York City to become "the most sustainable big city in the world and a global leader in the fight against climate change." <sup>2</sup>
- 2. New York City to reduce its greenhouse gas emissions 80 percent from the 2005 levels by 2050 (80 X 50 goal). <sup>2</sup>

The next year, 2016, the City followed up with a roadmap, *New York City's Roadmap to 80 X 50*, <sup>3</sup> that outlines the steps that are necessary to realize the 80 X 50 goal. In assembling the roadmap, the City used the most advanced technologies and analyses to device greenhouse gas (GHG) emission reduction strategies for the City's buildings, energy, waste, and transportation sectors. These strategies include programs, legislations, initiatives and policies targeted to make city buildings and fleet more energy efficient, and to transition from fossil fuels to renewable fuels and electric systems.

The roadmap delineates that in order to achieve its 80 X 50 goals the City must expediate its efforts to: 3

- Make buildings significantly more energy efficient,
- Replace many fossil fuel-based heating and hot water systems in buildings with renewable or high efficiency electric systems,
- Transition towards a renewables-based electric grid,
- Reduce the number of miles driven in New York City while replacing remaining vehicles to zero-emissions vehicles, and
- Achieve the goal of Zero Waste to landfills.

In December of 2017, in accordance with Local Law 22 of 2008, <sup>4</sup> the City released the citywide/city government greenhouse gas emissions inventory report for the calendar year of 2016, *Inventory of New York City Greenhouse Gas Emissions in 2016*. <sup>5</sup> The report stated, "... energy used in buildings is by far the largest source of emissions in City Government, generating 65% (1.8 MtCO2e) of City Government emissions."

Stationary energy (e.g., buildings), transportation, and waste sectors are the primary sources of the citywide GHG emissions in New York City. More specifically, the GHG emission inventory for 2016 <sup>5</sup> concluded that the



building sector remains the highest contributor with 66% of the total Citywide GHG emissions and 65% of the city government emissions.

In its *Progress Report-NYC Carbon Challenge* released in April 2018, <sup>6</sup> the City stated, "*In New York City, close to 70 percent of citywide GHG emissions can be attributed to the energy used to heat, power, and cool buildings.*" <sup>6</sup> Further, it reasoned that to achieve the 80 X 50 GHG emission goals, the efforts to replace fossil fuels used for heating the buildings with "*renewable or more efficient electric systems*" must proceed at a faster rate.

In line with the above, The City is looking at the potential of replacing the fossil heating fuels used in city government buildings with renewable diesel (RD).

Renewable diesel (RD) - also known as green diesel, hydrogenated vegetable oil (HVO), and hydrocarbon diesel among other names- is a drop-in replacement for diesel that is derived from animal fats and vegetable oils. Renewable diesel (RD) is an advanced biofuel that uses the same feedstock as biodiesel. However, RD differs from biodiesel in that its chemical structure is very similar to that of ultra-low sulfur diesel (ULSD) and contains no fatty acid methyl esters (FAME), such as biodiesel does. As an added benefit, HD is free of sulfur, aromatics and oxygen.

The Internal Revenue Service (IRS), <u>Internal Revenue</u>: <u>Bulleting 2001-17 dated April 23, 2007- Notice 2007-31-Section 2</u>, <sup>7</sup> defines hydrogenation derived renewable diesel (HDRD) as diesel fuel that:

- i. Is derived from biomass through a thermal depolymerization process, which is a process by which long chains of organic material are decomposed into short hydrocarbon chains;
- ii. meets the registration requirements for fuels and fuel additives established by the Environmental Protection Agency (EPA) under section 211 of the Clean Air Act;
- iii. meets the requirements of the American Society of Testing and Materials (ASTM) <u>D975- Standard Specification for Diesel Fuel Oil (https://www.astm.org/Standards/D975.htm)</u>, or <u>D396- Standard Specification for Fuel Oils (https://www.astm.org/Standards/D396.htm)</u>.

Further, the U.S. Department of Agriculture (USDA) has affirmed that "<u>Renewable diesel can be used in any proportion in diesel or heating oil.</u>" §

Concerning renewable diesel, the following statements are noteworthy:

- Renewable diesel (RD) is chemically similar to ultra-low sulfur diesel (ULSD). <sup>9</sup> Therefore, it is fully fungible and can be used in all existing diesel fueling infrastructure with no modifications.
- Renewable diesel (RD) can be blended with diesel and biodiesel in any proportion.
- Renewable diesel (RD) is produced from 100% renewable and sustainable feedstock; 10
- Renewable diesel (RD) passed EPA's Clean Air Health testing requirements. 11
- Renewable diesel (RD) reduces life-cycle greenhouse gas (GHG) emissions by up to 80% when compared to petroleum diesel; <sup>10</sup>
- The California Air Resources Board (CARB) has certified renewable diesel's pathways with very low carbon intensity (CI) scores, as low as 16.89 gCO<sub>2</sub>e/MJ for "used cooking oil" (UCO) feedstock. <sup>12</sup>



• The California Environmental Protection Agency conducted a study that tested renewable diesel in heavy duty diesel engines and released the results in May 2015, *Staff Report Multimedia Evaluation of Renewable Diesel*. <sup>13</sup> that showed emission reductions of 30% in particulate matter (PM), 10% in nitrogen oxides (NOx), 5% total hydrocarbons (THC), and 10% in carbon monoxide (CO) in the tailpipe emissions when compared to petroleum diesel.

In addition, because renewable diesel is composed of straight chain of hydrocarbons, it does not have the adverse effects of biodiesel (FAME) - like storage stability/shelf life problems, increased NOx emissions, strong solvent properties and challenging cold properties.

The use of renewable diesel in the transportation sector has already been effectively adopted by several municipalities throughout the world and in the US, with California leading this effort in the US West Coast.

In the East Coast, New York City, in its quest to reduce the City's GHG emissions, is spearheading the implementation of renewable diesel (RD). In 2018, DCAS NYC Fleet successfully conducted a pilot devised to assess the use of renewable diesel (RD) by municipal fleet. For the pilot, close to one million gallons of RD were stored/dispensed from city diesel stations to fuel about 1,000 city vehicles over a six-month period. The findings showed that renewable diesel (RD) met all the City's expectations, such as performance and carbon reduction targets. <sup>64</sup> As a result, the City is working on implementing a contract that would facilitate the purchase of RD and RD blends- i.e., RD/diesel, RD/biodiesel, and RD/diesel/biodiesel- as a transportation fuels by city agencies. The contract is expected to go into effect in 2019.

In an effort to further reduce the air pollutants in NYC and in response to the findings documented in the "*Progress Report-NYC Carbon Challenge*" published by the Mayor's Office of Sustainability, which stated "*In New York City, close to 70 percent of citywide GHG emissions can be attributed to the energy used to heat, power, and cool buildings,*" <sup>6</sup> the DCAS NYC Fleet is putting forward an unprecedented strategy that replaces the fossil fuels that are currently being burned to heat-up city buildings with 100% sustainable renewable diesel (RD) fuel that delivers significant emission reductions when compared to conventional diesel.

As of today, the use of renewable diesel (RD) has been directed almost exclusively to the transportation sector in the US and internationally. However, to expand the carbon emission reduction benefits that renewable diesel offers to other sectors that burn fossil fuels as sources of energy- such as residential and commercial heating-follows a natural progression in the pursuit for a better environment. To that end, the first-of-its-kind strategy presented in this study would turn NYC into the worldwide test-bed for the use of renewable diesel as a heating fuel for buildings.

This study shows that there is potential for using renewable diesel and renewable diesel blends as heating fuels for buildings, and that doing so would bring significant emission reductions that would help NYC achieve its 80X50 emission goal. In support of this effort, this study includes a technical overview of renewable diesel, technical papers and publications from the industry and well-recognized technical and governmental institutions, and relevant news articles.



#### INTRODUCTION

The City of New York recognizes the eminent threats that global warming and climate change pose to human health and the environment in local communities and around the world. In addition, the City also acknowledges the urgent need for all humanity to reduce its greenhouse gas (GHG) emissions that are causing harmful warming of the atmosphere and surface of the Earth. For these reasons, the City of New York is committed to reducing its GHG emissions by 80% below the 2005 levels by the year 2050 (80 X 50), diminishing this way, its carbon footprint and achieving net zero carbon dioxide (CO<sub>2</sub>) emissions- carbon neutrality. <sup>14</sup>

In 2014, the City codified its "80 X 50" GHG emission reduction commitment into permanent Local Law No. 66, which amended "the administrative code of the City of New York, in relation to reducing greenhouse gases by eighty percent by two thousand fifty." <sup>15</sup> In effect, Local Law No. 66 of 2014 amplified the City's Local Law No. 22 of 2008's GHG emission reduction target of 30% by year 2030 <sup>4</sup> to 80% GHG emission reduction citywide by year 2050.

Subsequently, in 2016, the City released its "New York City's Roadmap to 80 x 50," <sup>3</sup> which laid-out the next steps to achieve of 80 X 50 across all New York City's buildings, transportation, energy supply, and waste sectors. The roadmap was generated in conjunction with stakeholders and applied leading-edge analysis to generate a set of actions, strategies, and initiatives for each sector to mitigate GHG emissions from the burning of fossil fuels and from waste treatment.

That same year, on April 22, 2016, 196 countries, including the United States, signed the <u>Paris Agreement</u> <sup>16</sup> that would go in effect on November 4, 2016. By signing the Paris Agreement, all signatory countries committed to put forward their best efforts to avoid dangerous changes in the climate. The agreement establishes a global action plan to limit global average temperature warming for this century to 2°C (3.6°F) above pre-industrial levels and to pursue efforts to limit its rise to 1.5°C (2.7°F).

However, on June 1, 2017, President Trump announced the withdrawal of the United States from the <u>Paris</u> <u>Agreement</u>, <sup>16</sup> stating that "the Paris Accord is very unfair, at the highest level, to the United States." <sup>17</sup>

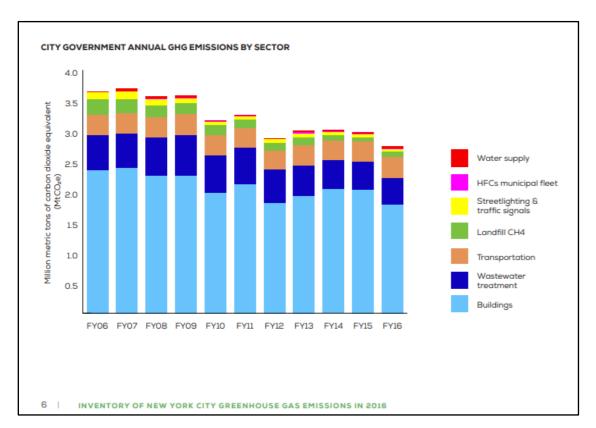
Nevertheless, the City of New York remained committed to the Paris Agreement and the next day, on June 2, 2017, Mayor de Blasio signed Executive Order No. 26, *Climate Action Executive Order*, <sup>18</sup> which reaffirmed the City's commitment to the principles and goals of the agreement. As such, the City is to take actions towards limiting the rise of the average temperature to 2°C (3.6°F) above pre-industrial levels, while pursuing efforts to limit it to 1.5°C.

Recognizing that to be in line with the Paris Agreement, the New York City's 80 X 50 goals needed to be aligned with the global warming 1.5°C (2.7°F) temperature increase limit. For this, it was determined that the City needed to accelerate its progress towards its 80 X 50 goals and implement a subset of its 80 X 50 strategies by 2020. Consequently, in September 2017, the City released its 1.5 °C Aligning New York City with the Paris Climate Agreement 19 plan, which sets out the pace, scale, and impact of the actions that need to be in place by 2020.



Previously, in December of 2013, the City of New York enacted Local Law 107 of 2013 to amend its administrative code by adding a new subsection i that require the use biodiesel (B5) in City owned municipal buildings. New Subsection i stated: "Use of biodiesel for heating purposes by city buildings. (1) After October first, two 2 thousand fourteen, all no. 2, no. 4 and no. 6 heating oil purchased for use in any building owned by the city shall be bioheating fuel containing not less than five percent biodiesel (B5) by volume except that the provisions of this subdivision shall not apply to the use of emergency generators."

In December of 2017, in accordance with Local Law 22 of 2008, <sup>4</sup> the City released the citywide/city government greenhouse gas emissions inventory report for the calendar year of 2016, *Inventory of New York City Greenhouse Gas Emissions in 2016*. <sup>5</sup> The report stated, "... energy used in buildings is by far the largest source of emissions in City Government, generating 65% (1.8 MtCO<sub>2</sub>e) of City Government emissions." This indicated that the burning of fossil fuels to heat city buildings and provide hot water is the leading source of GHG emissions in city government, surpassing GHG emissions from the wastewater treatment (16% GHG emission), and the transportation (12 % GHG emission) sectors. The figure below from the report clearly shows that the energy used in buildings was the predominant cause of GHG emissions in City Government:



Source: The City of New York- Inventory of the New York City Greenhouse Gas Emissions in 2016, December 2017 https://www1.nyc.gov/assets/sustainability/downloads/pdf/publications/GHG%20Inventory%20Report%20Emission%20Year%202016.pdf

According to the data presented on the <u>Inventory of New York City Greenhouse Gas Emissions in 2016</u> <sup>5</sup> report, the burning of diesel fuels by city buildings released 241,396 tCO<sub>2</sub>e, or 14% of the total city building GHG emissions, during FY 2016, following building electricity with 48% and natural gas with 33%.



City Government Building GHG Emission Summary 5		
Building Sector	FY 2016 - tCO2e 5	
#2 diesel fuel oil	98,669	
#4 diesel fuel oil	142,242	
#6 diesel fuel oil	485	
Biodiesel	55	
Electricity	848,782	
Kerosene		
Natural gas	591,022	
Propane	122	
Steam	84,639	
Total City Buildings GHG Emissions=	1,766,016	
City Government Building GHG Emission	1 Summary <sup>5</sup>	
- Diesel Fuels -		
#2 diesel fuel oil	98,669	
#4 diesel fuel oil	142,242	
#6 diesel fuel oil	485	
Diesel Fuel GHG Emissions from City Buildings=	241,396	
% Diesel Fuel GHG Emissions from City Buildings=	14%	
Note: tCO2e = Tonnes of carbon dioxide equivalent (CO2e)		

Source: The City of New York-Inventory of New York City Greenhouse Gas Emissions in 2016 5

 $\underline{https://www1.nyc.gov/assets/sustainability/downloads/pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Emission\%20Year\%202016.pdf/publications/GHG\%20Inventory\%20Report\%20Year\%20Ye$ 

Based on CARB's approved pathways <sup>12</sup> for renewable diesel (RD), the substitution of diesel fuel by renewable diesel may reduce lifecycle GHG emissions by as much as 83%. The substitution should be undetectable/unnoticeable since the chemical structure of renewable diesel is very similar to that of conventional diesel.

Moreover, when renewable diesel (RD) is used instead of diesel fuel, fine particles (PM) emissions can be reduced on average by 33%, nitrogen oxide (NOx) emissions by 9%, hydrocarbon (HC) emissions by 30%, carbon monoxide (CO) emissions by 24%. <sup>10</sup>

For added consideration, both the Internal Revenue Service (IRS) <sup>7</sup> and the Department of Agriculture (USDA) <sup>8</sup> recognize that renewable diesel (RD) can be used as a heating oil as well as transportation fuel.



#### **BACKGROUND**

#### **General Background:**

Human activities, specifically the burning of fossil fuels and deforestation, are releasing unprecedented amounts of greenhouse gases into the atmosphere. As the concentrations of greenhouse gases increase in the atmosphere, their combined effect acts as a thermal blanket warming the surface of the Earth.

Like greenhouses, greenhouse gases (GHGs) let the incoming sunlight passed through the atmosphere, but act as a thermal shield by effectively absorbing some of the outgoing solar energy and reradiating it back to the Earth's surface. Thus, preventing the outgoing solar energy from leaving the Earth and escaping into space. In the end, about 30% of the incoming solar radiation goes back into space as it is reflected back by the clouds, aerosols, and the surface of Earth. <sup>20</sup>

Greenhouse gases either occur naturally and are produced by human activities. Naturally occurring greenhouse gases are necessary for sustaining life on Earth as they keep its surface temperature suitable for living things. Without the greenhouse gases, the average temperature of the surface of the Earth would be about 0°F (-18°C) instead the warmer temperature of 59°F (15°C). 20, 21

The table below lists the most abundant gases in the Earth's atmosphere by percent volume:

Chemical Composition of Earth's Atmosphere			
Name	Chemical Formula	Percent Volume (%)	Residence Time in the Earth's Atmosphere <sup>22</sup>
Nitrogen	$N_2$	$78.08 \frac{22}{23}$	$10^6$ to $10^7$ years
Oxygen	$O_2$	$20.95 \frac{22}{23}$	$3^3$ to $10^3$ years
Argon	Ar	$0.93^{\frac{22}{23}}$	Forever
Water Vapor	$H_2O$	0 to $4^{\frac{22}{23}}$	10 days
Carbon Dioxide	$CO_2$	$0.0385^{\frac{22}{2}}$	2 to 10 years
Neon	Ne	$0.0018 \frac{22 \cdot 23}{}$	Forever
Helium	Не	$0.0005 \frac{22 \cdot 23}{}$	10 <sup>6</sup> years
Methane	CH <sub>4</sub>	$0.00018 \frac{22 \cdot 23}{}$	2 to 10 years
Krypton	Kr	0.00011 <sup>22</sup>	Forever
Hydrogen	$H_2$	0.00005	4 to 8 years
Nitrous Oxide	$N_2O$	$0.000033^{\frac{22}{23}}$	5 to 200 years
Carbon Monoxide	СО	$0.000005$ to $0.000020^{22}$	60 to 200 days
Xenon	Xe	$0.0000087^{22}$	Forever
Ozone	$O_3$	$0.000004^{23}$	
Chlorofluorocarbons, Hydrofluorocarbons, others	CFCs, HCFCs and HFCs, others	Traces	≤ a few second to forever

Even though our atmosphere is primarily composed of nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), and argon (Ar), these gases do not contribute to the greenhouse effect and are not greenhouse gases. This is because they are mostly unaffected by infrared radiation (infrared light).



#### **Gases, Molecular Science Overview:**

Greenhouse gases are composed of molecules that can absorb and re-emit energy from infrared radiation. Each molecule consists of atoms that have a nucleus with electrons orbiting around it, much like a sun in the center of a solar system. When two atoms combined, their nuclei shared orbitals and some of their electrons fall into these orbitals creating a chemical bond that hold the two atoms together. The chemical bond works as a spring that allows the atom to come closer together or move farther apart. A molecule can be composed of more than two atoms, and an atom can be bonded to one or more atoms.

When a greenhouse gas molecule absorbs energy from infrared radiation, the energy from the infrared photons causes the molecule's chemical bonds to vibrate because it creates an imbalanced electric field. According to the *University of Chicago, Forecast- Chapter 4: Greenhouses Gases: University of Chicago, Forecast- Chapter 4: Greenhouses Gases: "Changing the electric field is how greenhouse gases interact with IR light."* <sup>24</sup> This section further says that the molecule must be electrically "lopsided" (asymmetrical) to absorb or create infrared light. Hence, molecules contribute to the greenhouse effect when they absorb infrared energy and vibrate in such way as to create an imbalance (asymmetry) in their electric fields. Some time later, the molecule releases the absorbed energy to become more stable.

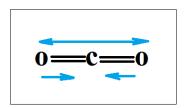
Nitrogen (N2) and oxygen (O2) are not greenhouse gases because they are composed of symmetrical molecules with two identical atoms of the same element, and there is no difference in the electric field on either side of the molecules. For these molecules, the vibrations resulting from the absorption of energy are symmetrical, with atoms moving closer or away from each other and do not create an imbalance in their electric fields. In general, homodiatomic molecules, which are composed of two atoms of the same element, are not greenhouse gases. Further, monoatomic molecules, such are argon (Ar), are not greenhouse gases either because they are unaffected by infrared light (IR) since they do not have vibrational modes.

Some heteroatomic molecules, e.g. Carbon monoxide (CO), hydrogen chloride (HCl), and nitrogen oxide (NO), do exhibit some greenhouse properties but they are not found in great quantities in the atmosphere because of they are very reactive and soluble. Consequently, their contribution to the greenhouse gas effect is very minor.

More Complicated molecules, such as molecules with three or more atoms, have more than one chemical bond, with each bond connecting no more than two atoms only. This means that triatomic molecules, and molecules with a higher number of atoms, may have several vibrational modes, including modes that affect the molecule's electric field.

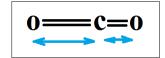
For example, the molecular structure of carbon dioxide ( $CO_2$ ) is a straight line with the carbon (C) atom in the middle and one oxygen (O) atom each side. The  $CO_2$  molecule can vibrate several ways:  $\frac{24}{3}$ 

• Symmetrical vibrational mode, towards and/or away from the carbon atom: This mode does not affect the CO<sub>2</sub> molecule's electric field:

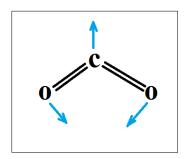




• Asymmetrical vibrational mode, towards and/or away from the carbon atom- where one oxygen atom goes farther away from the carbon atom while the other oxygen atom gets closer: This mode does slightly affect the CO<sub>2</sub> molecule electrical field, but its effect is insignificant for climate change:



• Bending Vibrational mode, the two oxygen atoms swing from side to side: This is the most important CO<sub>2</sub> vibrational mode affecting climate change. When the CO<sub>2</sub> molecule vibrates in its bending mode, the molecule is infrared active- meaning that it absorbs and emits infrared energy:



At the end, the amount of infrared energy that a molecule can absorb depends on many factors and varies significantly from molecule to molecule. Molecules with three atoms or more are infrared active at some point, <sup>24</sup> which is when they can absorb and emit photons as thermal energy. This results in the greenhouse effect that directly warms up the surface of the Earth and prevents part of the thermal radiation from escaping into space. The atmospheric gases that cause the greenhouse effect are commonly called "greenhouse gases."

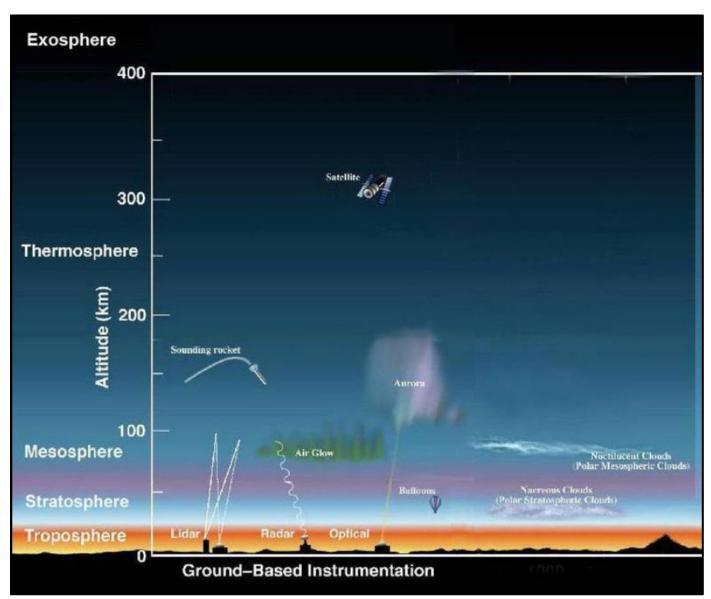
#### **Atmospheric Layers:**

According to the U.S. National Aeronautics and Space Administration (NASA), <sup>25</sup> the Earth's atmosphere is composed of the following six layers:

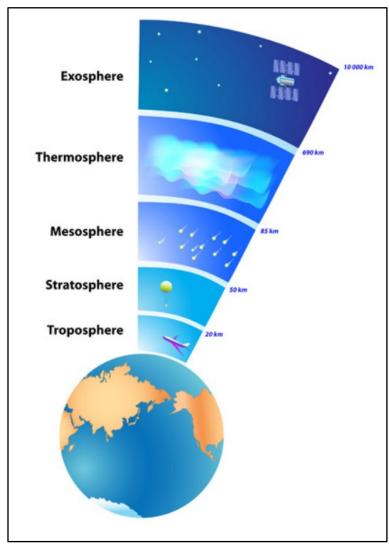
- <u>Troposphere:</u> The troposphere layer starts at the surface of the Earth and extends up to nine (9) miles (15 kilometers) high. It contains 75% of the atmosphere mass and is where most weather events occurred. The troposphere is wider around the equator.
- <u>Stratosphere</u>: The stratosphere is the second layer and extends up to 31 miles (50 kilometers). The ozone layer resides in this layer. In addition, this is the layer where volcanic gases affect the climate.



- <u>Mesosphere</u>: The mesosphere layer is after the stratosphere and it extends up to 53 miles (85 kilometers) above the surface of the Earth. Meteors burn up in this layer. Rocket powered aircrafts can access this layer.
- <u>Thermosphere</u>: The thermosphere layer starts just above the mesosphere and is extends up to 372 miles (600 kilometer) high and into the outer space. Satellites and the aurora are found in this layer.
- Exosphere: The exosphere is the highest layer. It extends from the top of the Thermosphere to up to 6,200 miles (100 kilometers) into space.



Source: NASA- Earth's Atmospheric Layers <sup>25</sup> (https://www.nasa.gov/mission\_pages/sunearth/science/atmosphere-layers2.html)



Source: Exploring the Environment - Global Climate Change (ETE-GCC) 26 (http://ete.cet.edu/gcc/?/volcanoes\_layers/)

#### **Global Warming Potential:**

As defined by the U. S. Environmental Protection Agency (EPA), <sup>19</sup> the global warming potential (GWP) of a greenhouse gas is "a quantified measure of the globally averaged relative radiative forcing impacts of a particular greenhouse gas." Further, GWP is specified as the accumulated radioactive forcing, direct and indirect, resulting from emitting 1 kilogram of gas within a 100-year time horizon, relative to reference gas CO<sub>2</sub>. Direct radioactive forcing occurs when the gas itself absorbs the energy. Indirect radioactive forcing is considered when the original gas chemically reacts to produce one or more greenhouse gases.

The GWP is function of the capacity of a greenhouse gas to absorb radiation (e.g., infrared energy), the spectral location of its absorbing wavelengths, and the lifetime of the of the gas in the atmosphere. So that, each greenhouse gas has its own unique capacity, which is its GWP measure, to contribute to greenhouse warming. For example, the GWP of CO<sub>2</sub> is one (1) over 100 years, since it is the reference gas. Methane's GWP is 28. This



means that the heat trapping capacity of methane is 28 times greater than that of carbon dioxide over the 100 years.

"Carbon dioxide equivalent" or "CO<sub>2</sub>e" is a common unit used to describe the amount of CO<sub>2</sub> that would deliver equivalent global warming impact for any quantity/type of greenhouse gas. In general, the CO<sub>2</sub>e is calculated by multiplying the mass of the greenhouse gas times its GWP value. For example, methane's GWP is 28. Thus, 1kg of methane would deliver 28kg CO<sub>2</sub>e, or 1kg X 28Kg CO<sub>2</sub>e.

As a special case, the GWP and radioactive forcing of water vapor has not been formally established yet. This is because several issues impede a direct calculation of its GWP. One of the main issues is that the "feedback loop" of the water vapor is not fully understood. As the temperature of the atmosphere rises, the warmer air would hold more water vapor. Since water vapor is a greenhouse gas, the higher concentration of water would then absorb more of the thermal radiation the emanates from the Earth's surface. This, in turn, makes the air warmer, which would lead to an increase in the water vapor concentration. Ultimately, as the water vapor concentration increases, clouds begin to form. Clouds can have a warming effect by trapping heat, and a cooling effect by blocking the sunlight. Difficulties in determining direct correlation to the water vapor's GWP are due in part to the limited understanding of the complexities of the feedback loops of water vapor, which play an intricate part in the calculation of its GWP.

#### Global Warming Potentials and Atmospheric Lifetimes (Years)

Gas	Atmospheric Lifetime	GWPa	
CO <sub>2</sub>	See footnote <sup>b</sup>	1	
CH <sub>4</sub> <sup>c</sup>	12	25	
N <sub>2</sub> O	114	298	
HFC-23	270	14,800	
HFC-32	4.9	675	
HFC-125	29	3,500	
HFC-134a	14	1,430	
HFC-143a	52	4,470	
HFC-152a	1.4	124	
HFC-227ea	34.2	3,220	
HFC-236fa	240	9,810	
HFC-4310mee	15.9	1,640	
CF <sub>4</sub>	50,000	7,390	
$C_2F_6$	10,000	12,200	
$C_4F_{10}$	2,600	8,860	
$C_6F_{14}$	3,200	9,300	
SF6	3,200	22,800	
NF <sub>3</sub>	740	17,200	

<sup>&</sup>lt;sup>a</sup> 100-year time horizon.

Source: U.S. Environmental Protection Agency (EPA)- Draft Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2017, February 2, 2019 19

https://www.epa.gov/ghgemissions/draft-inventory-us-greenhouse-gas-emissions-and-sinks-1990-2017

<sup>&</sup>lt;sup>b</sup> For a given amount of carbon dioxide emitted, some fraction of the atmospheric increase in concentration is quickly absorbed by the oceans and terrestrial vegetation, some fraction of the atmospheric increase will only slowly decrease over a number of years, and a small portion of the increase will remain for many centuries or more.

<sup>&</sup>lt;sup>c</sup> The GWP of CH<sub>4</sub> includes the direct effects and those indirect effects due to the production of tropospheric ozone and stratospheric water vapor. The indirect effect due to the production of CO<sub>2</sub> is not included. Source: (IPCC 2007)



#### **Climate Change and Global Warming:**

Greenhouse gases in the atmosphere act like an invisible blanket by entrapping some of the Earth's heat, and thus, preventing it from going into space. These gases later reemit the absorbed heat back to the Earth's surface, creating this way a greenhouse effect that warms-up the planet.

Greenhouse gases are critical to life on the planet because without the naturally occurring greenhouse effect caused by these gases the average temperature at the Earth's surface would be about 59 degrees Fahrenheit cooler, or 0°F (-18°C) instead of 59°F (15°C), and it would not support life as we know it. <sup>27</sup>

However, human activities, primarily the burning of fossil fuels and deforestation, have increased the natural concentration levels of the greenhouse gases in the atmosphere, mainly carbon dioxide and methane. Higher greenhouse gas concentrations lead to a rise in the greenhouse effect and that, in turn, results in an unnatural rapid increase in the average temperature of the planet's surface. This unusual increase in temperature is commonly referred to as 'global warming.'

Before the Industrial Revolution, Earth had experienced climate changes caused by natural events, e.g., minute variations in the Earth's orbit that affected the amount of sunlight the Earth received. However, many scientists believe that in recent decades, the Earth has been warming up much more rapidly than ever before and that this is most likely due to human activities. 31

The global average surface temperature has been steadily rising, and by the beginning of the 21<sup>st</sup> century, the Earth's average temperature was about 0.5°C higher than the long time average. The EPA reported that the temperature of the Earth's surface increased 1.8 degree Fahrenheit from 1901 to 2016. <sup>19</sup> New scientific models predict that the Earth will continue to warmup from around 2 to 6 degrees Celsius through the next century. <sup>31</sup>

Scientists believe that the continuously increasing concentrations of the greenhouse gases in the atmosphere, primarily carbon dioxide and methane, started at the beginning of the Industrial Revolution, back in the 1750s, and that the temperature of the Earth will continue to rise for decades to come unless human beings take measures to prevent it.

According to the EPA, <sup>33</sup> global warming is believed to be already affecting many areas of the planet. <sup>33</sup> For example, a higher percentage of the arctic ice is melting at a rate that has tripled in the last decade. Also, attributed to global warming is the finding that global sea level has risen in the past two decades at a rate that nearly doubles that of the last century. <sup>31</sup> This leads to an increased risk of coastal floating impacting coastal cities and communities that are located at/below sea level.

Furthermore, the impacts of climate change include: 31

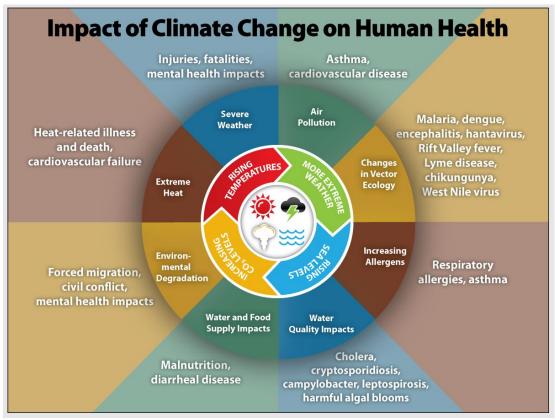
- Changes in precipitation, e.g., more rain falls and heavier downpours.
- Increased intensity and frequency of some types of extreme weather events, such as heat waves and severe droughts.
- The shrinking of the artic sea ice.
- Changes in ecosystems that may lengthen the frost-free season and shortening the corresponding growing season in some areas.



Overall, climate change impacts humanity is many ways:

- It affects the water we drink by changing the amount, timing and distribution of the precipitation, and decreasing summer runoffs that furnish our water supply. 34
- It also affects the food we eat because climate change not only impacts crop production, but it also affects livestock, fisheries and other segments of our food supply. 35
- It changes the air we breathe by decreasing the air's quality and creating several health risks,  $\frac{36}{100}$
- And, it plays a critical role on the weather we experience and our whole environment.

According to the U.S. Centers for Disease Control and Prevention (CDC), <sup>37</sup> climate change, coupled with natural and human-caused health stressors, impact human health such that existing health conditions may be more severe and new health treats will emerge. Health effects include increased respiratory and cardiovascular disease, higher number of injuries and premature death due to more severe weather events, and changes in the occurrences and geographical distribution on infectious diseases. <sup>37</sup>



Source: U.S. Centers for Disease Control and Prevention (CDC)- Climate Effects on Health <sup>37</sup> (https://www.cdc.gov/climateandhealth/effects/default.htm)

In 2016, the U.S. Global Change Research Program (USGCRP) published a report, *The Impact of Climate Change on Human Health in the United States- A Scientific Assessment*. <sup>32</sup> This report was the work of than 100 experts from eight (8) Federal agencies, including the Environmental Protection Agency (EPA), the Department of Health and Human Services (HHS), and the National Oceanic and Atmospheric Administration (NOAA), and documented their scientific assessments of how the climate change is affecting the heath of the Americans. One



of the reports's main findings was that "Climate change can therefore affect human health in two main ways: first, by changing the severity or frequency of health problems that are already affected by climate or weather factors; and second, by creating unprecedented or unanticipated health problems or health threats in places where they have not previously occurred." In view of this, the USGCRP's 2016 report concluded that: "Every American is vulnerable to the health impacts associated with climate change." <sup>32</sup> In the Report's Executive summary, the USGCRP presents the chart below that lists several examples of how the climate change impacts human health. <sup>32</sup>

Examples of Climate Impacts on Human Health				
	Climate Driver	Exposure	Health Outcome	Impact
Extreme Heat	More frequent, severe, prolonged heat events	Elevated temperatures	Heat-related death and illness	Rising temperatures will lead to an increase in heat-related deaths and illnesses.
Outdoor Air Quality	Increasing temperatures and changing precipitation patterns	Worsened air quality (ozone, particulate matter, and higher pollen counts)	Premature death, acute and chronic cardiovascular and respiratory illnesses	Rising temperatures and wildfires and decreasing precipitation will lead to increases in ozone and particulate matter, elevating the risks of cardiovascular and respiratory illnesses and death.
Flooding	Rising sea level and more frequent or intense extreme precipitation, hurricanes, and storm surge events	Contaminated water, debris, and disruptions to essential infrastructure	Drowning, injuries, mental health consequences, gastrointestinal and other illness	Increased coastal and inland flooding exposes populations to a range of negative health impacts before, during, and after events.
Vector-Borne Infection (Lyme Disease)	Changes in temperature extremes and seasonal weather patterns	Earlier and geographically expanded tick activity	Lyme disease	Ticks will show earlier seasonal activity and a generally northward range expansion, increasing risk of human exposure to Lyme disease-causing bacteria.
Water-Related Infection (Vibrio vulnificus)	Rising sea surface temperature, changes in precipi- tation and runoff affecting coastal salinity	Recreational water or shellfish contaminated with Vibrio vulnificus	Vibrio vulnificus induced diarrhea & intestinal illness, wound and blood- stream infections, death	Increases in water temperatures will alter timing and location of <i>Vibrio vulnificus</i> growth, increasing exposure and risk of waterborne illness.
Food-Related Infection (Salmonella)	Increases in temperature, humidity, and season length	Increased growth of pathogens, seasonal shifts in incidence of Salmonella exposure	Salmonella infection, gastrointestinal outbreaks	Rising temperatures increase Salmonella prevalence in food; longer seasons and warming winters increase risk of exposure and infection.
Mental Health and Well-Being	Climate change impacts, especially extreme weather	Level of exposure to traumatic events, like disasters	Distress, grief, behavioral health disorders, social impacts, resilience	Changes in exposure to climate- or weather-related disasters cause or exacerbate stress and mental health consequences, with greater risk for certain populations.

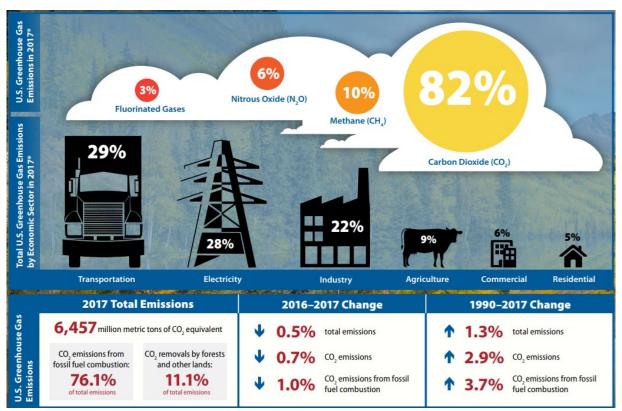


#### **Most important Greenhouse Gases:**

In the United States, the U.S. Department of Environmental Protection Agency (EPA) has identified the following primary greenhouse gases: <sup>19</sup>

- Water Vapor (H<sub>2</sub>O).
- Carbon Dioxide (C<sub>2</sub>O).
- Methane (CH<sub>4</sub>).
- Nitrous Oxide (N<sub>2</sub>O).
- Ozone (O<sub>3</sub>).
- Fluorinated Gases:
  - o Hydrofluorocarbons (HFCs),
  - o perfluorocarbons (PFCs),
  - o sulfur hexafluoride (SF<sub>6</sub>),
  - o nitrogen trifluoride (NF<sub>3</sub>),

In its <u>Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2017</u>, published on February 2, 2019, <sup>19</sup> the US Environmental Protection Agency (EPA) stated "The most important greenhouse gases directly emitted by humans include carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), nitrous oxide ( $N_2O$ ), and several other fluorine-containing halogenated substances." The EPA presented the following overview of the greenhouse gas emissions in the United States:



Source: U.S. Environmental Protection Agency - *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-201, February 2, 2019* https://www.epa.gov/ghgemissions/draft-inventory-us-greenhouse-gas-emissions-and-sinks-1990-2017



The effect that each one of greenhouse gases has on the Earth's climate change depends on:

- 1. The concentration of each gas in the atmosphere.
- 2. How long each gas stays in the atmosphere- its atmospheric lifetime.
- 3. How much each gas contributes to the global warming of the surface of the Earth, which is determined by its global warming potential (GWP).

Carbon monoxide (CO) is not regarded as a greenhouse gas because it is a poor absorber of infrared energy. However, though Carbon monoxide is short-lived (about one month), its presence in the atmosphere indirectly affects global warming because carbon monoxide (CO) reacts with certain atmospheric chemicals that destroy and remove methane and tropospheric ozone from the atmosphere. By doing so, carbon monoxide (CO) helps elevate the atmospheric concentrations of methane and tropospheric ozone, which in turn affects the warming of the Earth

#### Water Vapor (H2O)

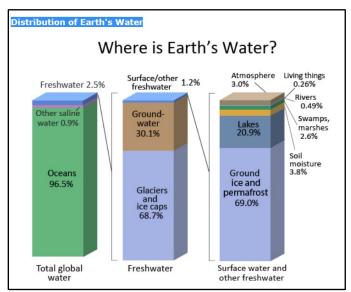
Water vapor in the Earth's atmosphere results from natural causes, such as the evaporation of water from water bodies, e.g. oceans, seas, and lakes, and from human activities, such as irrigation and domestic water use.

The man-made (anthropogenic) water vapor emissions are much smaller than the natural emissions from ground water storage areas (oceans, reservoirs, rivers, soil, etc.). So that, the effect of anthropogenic water vapor emissions on global climate is inconsequential. 19

Water vapor is the most powerful contributor to the natural greenhouse effect in the Earth's surface. It differs from the other greenhouse gases in that it does not decay, but at high enough concentrations, it condenses into clouds and falls back to the Earth's surface in the form of rain/snow/ice, which can cause a cooling effect. The concentration of water vapor in the atmosphere (troposphere) depends on the temperature of the air and the availability of water on the Earth's surface. The air's temperature limits the maximum amount of water vapor that can be in the atmosphere without condensation. The highest concentration of water vapor – air moisture – is found along the Equator line and rain forests. Areas with the lowest air moisture content include deserts and polar regions. On average, the lifetime of water vapor in the troposphere, which is where most of the water vapor resides, is about 10 days. <sup>19</sup>

Water vapor also serves as a heat transfer agent between the Earth's surface and the troposphere layer. This occurs when liquid water at the surface absorbs heat to evaporate (latent heat of vaporization). The water vapor then travels through the troposphere where it releases the latent heat of vaporization upon its condensation.





Source: U.S. Geological Survey's (USGS) Water Science School- *The World's Water, Distribution of Earth's Water* <sup>28</sup> (https://water.usgs.gov/edu/earthwherewater.html)

Water vapor is the Earth's most abundant greenhouse gas, but its overall contribution to global warming, or global-warming potential (GWP), is yet to be determined.

#### Carbon Dioxide (CO2)

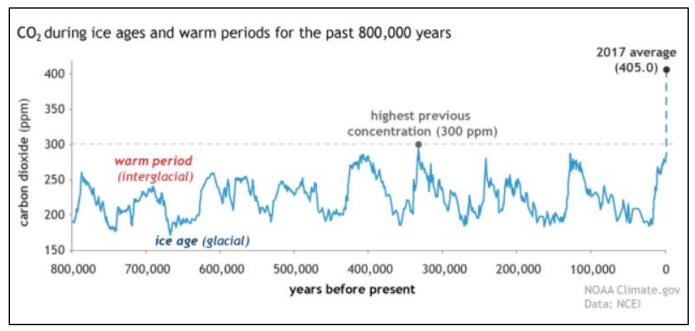
As reported by the U.S. Environmental Protection Agency (EPA), carbon dioxide (CO<sub>2</sub>) accounted for 81% of the greenhouse emissions in the United States in 2016. <sup>29</sup> Carbon dioxide is the fifth most abundant gas in the Earth's atmosphere - after nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), argon (Ar) and water vapor (H<sub>2</sub>O). It occurs naturally and through human activities, and it is vital to the Earth's carbon cycle, through which carbon is removed by some natural activities (such as photosynthesis and the formation limestones) and released back into the atmosphere by other natural processes, e.g. respiration and the decomposition of organic matter.

Nationally, the US Environmental Protection Agency (EPA) in its annual report that compiled the total greenhouse gas emissions for all man-made sources in the United States, <u>Draft Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2017</u> <sup>16</sup> reported that the principal greenhouse gas (GHG) emitted from human activities in the United States is carbon dioxide (CO<sub>2</sub>) accounting for 81% of the total GHG emissions. The CO<sub>2</sub> gas is mostly released to the atmosphere by the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation.

According to the U.S. National Oceanic and Atmospheric Administration (NOAA) and the American Meteorological Society, the atmospheric carbon dioxide concentrations are rising because the burning of fossil fuels (such as coal and oil) by human beings. In 2017, the global average atmospheric carbon dioxide concentration was estimated to be  $405.0 \pm 0.1$  parts per million (ppm). Going back 800,000 years before the present, the highest concentration carbon dioxide in the atmosphere was less than 300 ppm. By burning fossil



fuels, we are returning to the atmosphere millions of years' worth of the carbon dioxide that was removed by the plants through the photosynthesis process in just a few years. <sup>38</sup> The following chart from NOAA Climate.gov shows the global atmospheric carbon dioxide (CO<sub>2</sub>) concentrations for the past 800,000 years, based on EPICA (European Project for Ice Coring in Antarctica) data.



Source: U.S. Department of Commerce- National Oceanic and Atmospheric Administration (NOAA), *Climate Change: Atmospheric Carbon Dioxide* <sup>38</sup>
(https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide)

Carbon dioxide (CO<sub>2</sub>) is the primary greenhouse gas emitted by human activities (anthropogenic). Even though it absorbs less heat per molecule than methane and nitrous oxide, it stays in the much longer and it is more abundant than those two greenhouse gases. When compared to water vapor, carbon dioxide (CO<sub>2</sub>) is less abundant, but it absorbs energy at wavelengths that water vapor does not. This means that carbon dioxide contributes to the greenhouse effect, and the warming of the Earth, in a very distinctive way. Two-thirds (2/3) of the total increases of the Earth's energy, which causes the warning of the planet, has been attributed to the rise in the concentration of atmospheric carbon dioxide (CO<sub>2</sub>). 38

In addition, carbon dioxide (CO<sub>2</sub>) dissolves into the seawaters and a series of chemical reactions occur resulting on increased production of carbonic acid and thus, unnaturally decreasing the pH of the Earth's surface ocean waters. This is called ocean acidification. As the seawaters become more acidic, it changes the ocean chemistry, and this affects marine life. For example, calcium carbonate minerals, which are critical for the shell structures of oysters, clams, and for coral skeletons, are less abundant as the waters become more acidic. <sup>38</sup>

MOAA predicts that the atmospheric carbon dioxide (CO<sub>2</sub>) concentration will reach 900 ppm by the end of this century if the demand for fossil fuel energy continues to grow. <sup>38</sup> Further, The Intergovernmental Panel on Climate Change (IPCC) in its fifth (5<sup>th</sup>) Assessment Report, *Climate Change-Synthesis Report*, published in 2015 stated "Cumulative emissions of CO<sub>2</sub> largely determine global mean surface warming by the late 21st century and beyond." <sup>30</sup>



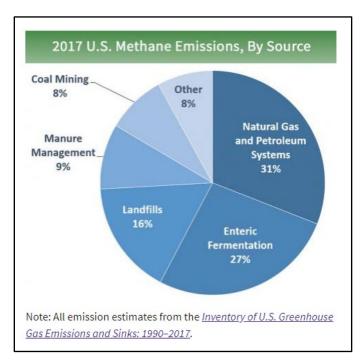
#### Methane (CH<sub>4</sub>)

Methane is the simplest hydrocarbon, consisting of one carbon atom and four hydrogen (CH<sub>4</sub>). It is also the second most important greenhouse gas and accounted for about 10% of the greenhouse gases produced in the United States in 2017. <sup>19</sup> Methane (CH<sub>4</sub>) lasts about 10 to 12 years in the atmosphere. Eventually, methane (CH<sub>4</sub>) is removed from the atmosphere by chemical reactions, mainly the reaction of methane with the hydroxyl radical (·OH). Subsequently, the methane/ hydroxyl radical reaction leads to a long series of chemical reactions that convert the methane into CO<sub>2</sub> and other compounds, which are removed by precipitation or surface's uptake. In a way, the hydroxyl radicals act like cleansers that scrub the atmosphere of methane pollutants.

Though methane's lifetime ( $\sim$ 10 to 12 years) in the Earth's atmosphere is much shorter than that of carbon dioxide (carbon dioxide can remain in the atmosphere for thousand years), it is a potent and very effective greenhouse gas. Methane's global warming potential (GWP) averaged is 28 -36 over 100 years.  $\frac{29, 40}{100}$  This means that molecule by molecule (or ounce by ounce), methane at the very least entraps 28 times more atmospheric heat, and causes 28 times more warming, than carbon dioxide over a 100-year period.  $\frac{39}{100}$ 

Methane is emitted to the atmosphere by natural and anthropogenic sources. The Intergovernmental Panel on Climate Change (IPCC) reported in its 2015, <u>The Synthesis Report (SYR) of the IPCC Fifth Assessment Report (AR5):</u> <u>Climate Change 2014 Synthesis Report,</u> <sup>30</sup> that globally, more than half, 50-65 percent of total methane emissions, are caused by human activities, such as the burning of fossil fuels, agriculture and waste disposal.

Regarding methane emissions in the United States, the U.S. Environmental Protection Agency (EPA) presented the following graph in its report *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2017*, that was published on February 2, 2019: <sup>19</sup>



Source: U.S. Environmental Protection Agency (EPA)- Overview of Greenhouse Gases, Methane emissions <sup>29</sup> https://www.epa.gov/ghgemissions/overview-greenhouse-gases#methane



The global concentration of methane has increased 164% since 1750, from 700 ppb (parts per billion) in preindustrial (prior to 1750) to 1,849 ppb in 2017. Methane's atmospheric accumulation flatten out, and remained virtually constant, near-zero growth, during the decade before 2006. However, it started to rise again in 2007 and has continue to increase at a rate of 7 ppb/year since then. <sup>19,41</sup>

In the United states, natural gas and petroleum (fossil fuel) systems were the main sources of anthropogenic methane (CH<sub>4</sub>) emissions with 31% in 2017. Methane (CH<sub>4</sub>) is the main component of natural gas and is released to the atmosphere during the processing and use of natural gas. Methane is also generated through the production, processing, storage, transmission, and distribution of fossil fuels. <sup>29</sup>

The second largest source of methane emissions from human related activities in the United States is enteric fermentation, which is the natural digestive process of domesticated and wild ruminant animals (e.g., cattle, deer, goats and camels). During the enteric fermentation digestive process, plant materials (e.g., celluloses, fibers and sugars) that the animals have eaten are decomposed and fermented by microorganisms into simple molecules that can then be absorbed into the bloodstream of the animal. Enteric methane is one of the by-products of this digestive process, which is exhaled or belched by the animals, and accounts for 27% of the anthropogenic methane emissions in the United States. <sup>29</sup>

Municipal solid waste (MSW) Landfills and open dumps are also a source of human related methane emissions in the United States and accounted for 16% of these emissions in 2017. Methane is generated as a natural byproduct of the decomposition of organic waste under anaerobic (without oxygen) conditions. The amount of methane created depends on the quantity, moisture content of the waste materials, and local factors, such as climate and landfill design. <sup>42</sup>

In addition, methane is produced from by the microbial decomposition of the organic components of livestock manure under anaerobic (absence of oxygen) conditions. This occurs when large numbers of animals are restrained in a confined limited area, such as dairy farms, where manure is stored and managed in large piles or dispose of in lagoons and tanks. Livestock manure is mostly composed of organic materials and water, and methane is mainly emitted from the slurries and liquids that are formed during anaerobic decomposition of the organic manure. <sup>43</sup> Different manure treatment and storage methods affect how much of methane is produced. The EPA reported that manure management, mainly storage and land use, accounted for 9%- the fourth largest source - of the anthropogenic (human-related) methane in the United States in 2017. <sup>19</sup>

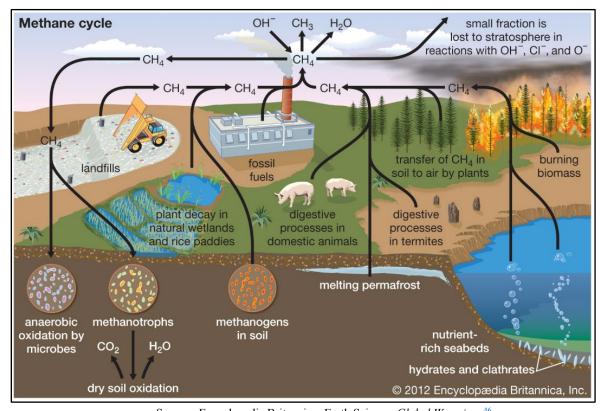
Coal mines are the fifth largest emitting source of methane emissions in the United States, accounting for 8% of these emissions in 2017. Coal mine methane (CMM) is mostly produced during mining operations in large/high-production, longwall underground active mines and released through the mine ventilation shafts and degasification wells. To a much lesser extent, methane is also released by surface and abandoned mines, and as fugitive methane when coal is handled and transported after mining. <sup>19</sup> 44

Other sources of methane emissions include rice cultivation, wetlands, wastewater treatment, and burning of biomass, e.g., crop residues and forest trees. Methane is also generated by termites as part of their normal digestive process, and it accounts for 11% of the world methane emissions from natural sources. <sup>45</sup> These sources captured the most of the remaining 8% of the total methane emissions in the United States during the year 2017 as reported by the EPA. <sup>19</sup>



Just like water, methane goes through a cycle where it is released into the atmosphere by numerous sources, removed/scrubbed from the atmosphere by various natural sinks, such as the hydroxyl radical (·OH) and soil uptake, and is released again to repeat the cycle. The methane cycle starts with microbes called 'methanogens' that reside in the soil and create methane. Methanotrophs are microorganisms in the soil that feed methane. In general, methane is released from the soil into the atmosphere when the methanogens create more methane than what the methanotrophs can consume. The released soil methane combines with methane from the other sources, increasing the atmospheric methane concentration.

Another source of atmospheric methane is methane crystals, Clathrates or methane hydrates, that form in the cold undersea sediments in the Arctic and Antarctic pole regions. These crystals contained molecules of methane surrounded by molecules of water. As the Earth warms up, the deep sediments start melting, releasing methane to the atmosphere.



Source: Encyclopedia Britannica- Earth Science, *Global Warming* 46 <a href="https://www.britannica.com/science/global-warming/Carbon-dioxide#ref1081189">https://www.britannica.com/science/global-warming/Carbon-dioxide#ref1081189</a>

Methane emissions have been increasing at a rate of about 25 trillion grams (1.1 million U.S. tons) per year since 2006. A team of scientist from the U.S. National Aeronautics and Space Administration (NASA) reported in January 2, 2018 that the recent rise in methane emissions is primarily caused by fossil fuels, mostly by oil, coal, and natural gas. The NASA team estimated that fossil fuels account for 17 trillion grams/year of the 25 trillion grams of increased methane emission rate since 2006. <sup>47</sup>



#### Nitrous Oxide (N2O)

Nitrous oxide ( $N_2O$ ) is the fourth most important greenhouse gas in the United States, accounting for about 6% of the greenhouse gas emissions in 2017. <sup>29</sup> Under normal conditions, nitrous oxide is a colorless, tasteless, odorless, non-flammable, mildly reactive, nontoxic gas that has many applications in the medical field, dentistry and surgery, such as an anesthetic and an analgesic.

Nitrous oxide (N<sub>2</sub>O) affects the nervous system in a similar manner as alcohol intoxication. In dentistry, nitrous oxide is commonly known as "laughing gas" because inhaling it would relax the patients. Care need to be taken that enough oxygen is supplied to the patient inhaling nitrous oxide; otherwise, it would result in asphyxia.

Nitrous oxide (N<sub>2</sub>O) is both a greenhouse gas and an ozone depleting gas. As a greenhouse gas, nitrous oxide is powerful, relentless, and very destructive to the ozone layer. It has a Global Warming Potential (GWP) of 298 based for a 100-year time horizon. This means that a single molecule of nitrous oxide (N<sub>2</sub>O) is nearly 300 times more effective as a greenhouse gas than a molecule of carbon dioxide (CO<sub>2</sub>). Further, nitrous oxide (N<sub>2</sub>O) has an atmospheric lifetime of 114 year, <sup>19</sup> and the atmosphere contains 1,000 times more carbon dioxide than nitrous oxide

Before the Industrial Revolution in the late 1700s, the concentration of nitrous oxide in the atmosphere was balanced and stayed at a safe level due to natural sinks. However, the atmospheric concentration of nitrous oxide has been on the rise for the last two (2) decades. This is mainly due to human activities that are creating emissions at much more faster rates than the Earth's sinks can remove them.

Nitrous oxide emissions are produced by both natural and human sources. Natural sources create about 60% of the global nitrous oxide emissions and human-related sources are responsible for the remaining 40%. <sup>19</sup> Today, nitrous oxide levels are the highest point that they have been in the last 800,000 years. <sup>48</sup>

Leading natural sources of nitrous oxide emissions include soils under vegetation, tundra ecosystems and oceans. The largest natural source of nitrous oxide is soil where nitrogen is removed by microorganism that break down the nitrogen in the soil and then release it into the atmosphere through the process of denitrification, which breaks apart nitrogen-containing elements and produces nitrogen gases, including nitrous oxide. Tropical forest soils are the main natural source of nitrous oxide emissions on Earth. <sup>50</sup>

Tundra ecosystems also release nitrous oxide to the atmosphere. Tundra ecosystems are treeless regions that reach extremely low temperatures, and have very little rainfall, poor nutrients, and short growing seasons. Dead organic materials, mostly containing nitrogen and phosphorous, serve as nutrients for shrubs, sedges, reindeer mosses, grasses and other plants that have adapted to these harsh conditions. The tundra ecosystems are separated into two (2) types, arctic tundra and alpine tundra.

The arctic tundra is in the northern hemisphere, encircling the North Pole. Arctic soils are estimated to be substantial sources of nitrous oxide emissions due to permafrost thawing. Because of climate change, the Arctic is warming at a rate almost twice as fast as the rest of the planet. As the arctic land rapidly warms-up, the permafrost layer below the surface is thawing. <sup>51</sup> This thawing is releasing massive amount of greenhouse gases, including nitrous oxide, from a vast pool of trapped gasses that have been collecting for thousands of years. A



recent <u>study by Harvard University</u> <sup>51</sup> concluded that "The warming Arctic permafrost may be releasing more nitrous oxide, a potent greenhouse gas, than previously thought."



Alpine tundra in the North Cascades of Washington, United States Source: Wikipedia at <a href="https://en.wikipedia.org/wiki/Tundra-">https://en.wikipedia.org/wiki/Tundra-</a>

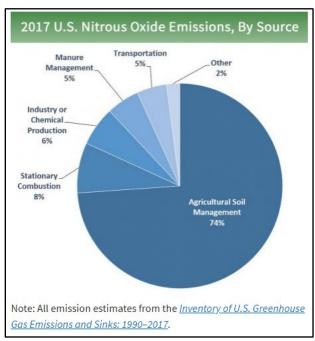


From left: alpine tundra in Mt. Rainier National Park, Washington; Dall Sheep in the Arctic National Wildlife Refuge, Alaska. Source: Berkeley University at <a href="https://ucmp.berkeley.edu/exhibits/biomes/tundra.php">https://ucmp.berkeley.edu/exhibits/biomes/tundra.php</a>

Oceans are an important natural source of nitrous oxide emissions. Microbes living in the ocean waters create these emissions through microbial activities in or around sinking particles, e.g., fecal pellets, that release nitrous oxide as a by-product. 35% of the natural nitrous oxide emissions, about 3.8 million tons of nitrous oxide per year, are attributed to microbial activities in the ocean water. <sup>52</sup>

Human activities (anthropogenic activities) are releasing unprecedented amounts of nitrous emissions to the atmosphere. The EPA's website <sup>29</sup> identifies agriculture, fuel combustion, wastewater management, and industrial processes as the chief sources of anthropogenic nitrous oxide emissions. <sup>29</sup>





Source: US Environmental Protection Agency (EPA)- Overview of Greenhouse Gases: Nitrous Oxide Emissions 29 https://www.epa.gov/ghgemissions/overview-greenhouse-gases#nitrous-oxide

The primary source of anthropogenic nitrous emissions is the enhanced microbial activity in agricultural soils. Specific activities such as application of synthetic and organic fertilizers, the growth of nitrogen-fixing crops, the draining of organic soil and irrigation practices are the foremost contributors. <sup>29</sup> The use of nitrogen-based fertilizers creates an imbalance between the extra nitrogen in the fertilizer and the plant intake. Fertilizers help plants grow, but the microbes in the soil also get to process extra nitrogen and release an increased amount of nitrous oxide.

Another agricultural source of nitrous oxide is the storage and handling of the manure left in the fields by livestock after grazing. The way in which livestock manure is managed for storage and handling affect how much nitrous oxide is released into the atmosphere. Manure management is responsible for 14% of the total agricultural greenhouse gas emissions in the United States. In addition, there are other agricultural sources, such as the burning of crop, which produce smaller quantities of nitrous oxide. <sup>29, 19</sup>

An important source of anthropogenic nitrous oxide is the combustion of fossil fuels in both the residential/commercial and transportation sectors. Nitrous oxide is a byproduct of the burning of fossil fuels in stationary as well as in mobile sources. In its report <u>Inventory of U.S. Greenhouse Gas Emissions and Sinks:</u> <u>1990–2017</u>, <sup>19</sup> the US EPA mentions that 8% of the total nitrous oxide emissions in 2017 in the United states emanated from stationary sources, such as residential or commercial, while the transportation sector accounted for about 5% of the total nitrous oxide emissions. The EPA points out that: "The amount of  $N_2O$  emitted from burning fuels depends on the type of fuel and combustion technology, maintenance, and operating practices." <sup>29</sup>

Nitrous oxide is also generated by industries as a byproduct of chemical reactions that occur during the production of chemicals, such as nitric acid. Industrial nitrous oxide emissions accounted for 5 about % of the total nitrous oxide emissions in the United states in 2017, and waste management contributed another 1.4%. 19



#### Ozone (O<sub>3</sub>)

Ozone (O<sub>3</sub>) is a highly reactive inorganic molecule composed of three oxygen atoms. It is a light blue gas, which condenses into a dark blue liquid, and it has a pungent smell. Ozone has two distinct purposes in the atmosphere, as a protective layer in the stratosphere and as a pollutant and one of the chief smog contributor at the Earth's ground-level.

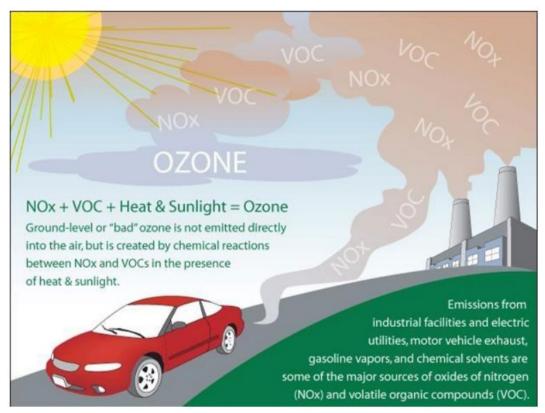
In the stratosphere, about 6 to 30 miles above in the upper atmosphere, ozone forms a protective layer that absorbs the damaging ultraviolet (UV) rays emitted by the sun, preventing harmful UV rays from reaching the surface of the Earth. Stratospheric ozone is formed naturally from the interaction of the ultraviolet (UV) radiation with the molecular oxygen (O<sub>2</sub>) in the air. However, manmade chemicals, such as chlorofluorocarbons (CFCs), are causing the stratospheric ozone layer to deplete, specially over the North and South poles. Recognizing this threat, the United States and 180 other countries adopted the <u>Montreal Protocol Treaty</u> in 1987 that aims at implementing measures to phase out the production and use of ozone-depleting chemicals. <sup>53</sup>

Ground-level ozone is created just above the Earth's surface when nitrogen oxides (NOx) (e.g., nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>)) and volatile organic compounds (VOCs), such as benzene and formaldehyde, react under the sunlight. Ozone is referred to as a secondary pollutant because it is formed from primary pollutants, NOx and VOCs. Both pollutants, nitrogen oxide (NOx) and volatile organic compounds (VOCs), come from natural sources and from human activities, mainly the burning of fossil fuels by vehicles, industrial/residential boilers, refineries, and chemical plants. <sup>54</sup>

Ground-level Ozone can have very harmful effects on human health when it reaches high concentrations in the air we breathe. Hot and sunny weather with stagnant air can lead to the ozone concentration to rise to unhealthy levels, which can irritate the respiratory system and cause the muscles in the airways to constrict resulting in shortness of breath and wheezing, especially on children, the elderly, and people of all ages who have lung diseases such as asthma, chronic bronchitis, and emphysema. Studies have found significant correlation between long term exposure to ozone and premature death. <sup>54</sup>

As per the Environmental Protection Agency (EPA), <sup>54</sup> ground-level ozone can affect human beings by:

- Making it more difficult to breathe deeply and vigorously.
- Causing shortness of breath, and pain when taking a deep breath.
- Causing coughing and sore or scratchy throat.
- Inflaming and damage the airways.
- Aggravating lung diseases such as asthma, emphysema, and chronic bronchitis.
- Increasing the frequency of asthma attacks.
- Making the lungs more susceptible to infection.
- Continuing to damage the lungs even when the symptoms have disappeared.
- Causing chronic obstructive pulmonary disease (COPD).



US Environmental Protection Agency (EPA)- *Ground-level Ozone Basics* 54 https://www.epa.gov/ground-level-ozone-pollution/ground-level-ozone-basics

The US Environmental Protection (EPA) developed Air Quality index (AQI) to help explain the effects of local air quality on public health. AQI values below 100 are considered are acceptable. Conversely, AQI values above 100 are unhealthy and the effects range from affecting sensitive groups of people to the entire communities, as the AQI values increase. 55

Air Quality Index (AQI) Values	Levels of Health Concern	Colors
When the AQI is in this range:	air quality conditions are:	as symbolized by this color:
0 to 50	Good	Green
51 to 100	Moderate	Yellow
101 to 150	Unhealthy for Sensitive Groups	Orange
151 to 200	Unhealthy	Red
201 to 300	Very Unhealthy	Purple
301 to 500	Hazardous	Maroon

Source: U.S. Environmental Protection Agency (EPA)- AirNow, *Air Quality Index (AQI) Basics* 55 <a href="https://airnow.gov/index.cfm?action=aqibasics.aqi">https://airnow.gov/index.cfm?action=aqibasics.aqi</a>



#### **Fluorinated Gases**

The Environmental Protection Agency (EPA) considers four (4) types of fluorinated greenhouse gases (F-gases). They are: Hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexaflouride (SF<sub>6</sub>) and nitrogen trifluoride (NF<sub>3</sub>). Fluorinated gases are synthetic and caused by human activities. There are no natural sources that produce fluorinated greenhouse gases. <sup>29</sup>

Although fluorinated greenhouse gases exist in the atmosphere in miniscule concentrations, they have considerable impact in climate change, such as global warming and increased precipitation occurrences. This is because fluorinated gases have high global warming potentials (GWPs)- up to about 23,000 that of carbon dioxide (CO<sub>2</sub>)- and thus, these gases are many times more powerful greenhouse gases than carbon dioxide. In addition, fluorinates greenhouse gases (F-gases) have very long atmospheric lifetimes. Subsequently, F-gases remain in the atmosphere for extensive periods time periods (centuries). <sup>29</sup>

# Properties of F-gases Chemical Formula: HFCs, PFCs, NF<sub>3</sub>, SF<sub>6</sub> Lifetime in Atmosphere: HFCs: up to 270 years PFCs: 2,600-50,000 years NF<sub>3</sub>: 740 years SF<sub>6</sub>: 3,200 years Global Warming Potential (100-year): HFCs: up to 14,800 PFCs: 7,390-12,200 NF<sub>3</sub>: 17,200 SF<sub>6</sub>: 22,800

Source: U.S. Environmental Protection Agency (EPA)- *Overview of Greenhouse Gases* <sup>29</sup> <u>https://www.epa.gov/ghgemissions/overview-greenhouse-gases</u>

Fluorinated gases have numerous uses in industry: 29

- \* Hydrofluorocarbons (HFCs) were developed to replace chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which are destroyers of the stratospheric ozone layer, in the refrigeration and insulated foam industries. They are utilized in commercial and industry refrigeration, air conditioners, fire extinguishers, aerosol propellants among other industries. Hydrofluorocarbons (HFCs) are released into the atmosphere through manufacturing processes, applications, leaks, and disposal of equipment that contain them.
- Perfluorocarbons (PFCs) are used in the electronics, cosmetics, and pharmaceutical industries. Aluminum production is the principal source of Perfluorocarbons (PFCs).
- Sulfur hexafluoride (SF<sub>6</sub>) is mainly used in magnesium processing, as an insulating gas semiconductor manufacturing, and as a tracer gas for the detection of leaks.



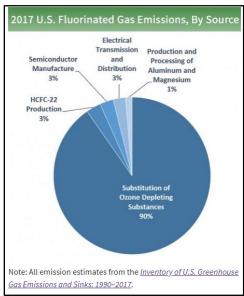
Nitrogen trifluoride (NF<sub>3</sub>) is released and utilized in the manufacturing of semi-conductors, new generation solar panels, flat-screen television sets, touch-sensitive screens, electronic processors.

According to the US Environmental Protection Agency (EPA), in the United States, fluorinated gas emissions increased 69.7 percent from 1990 to 2017. This surge was chiefly due to an increase in the use of hydrofluorocarbons (HFCs) as substitutes for ozone-depleting chemicals, mainly for chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). <sup>29</sup> Certain fluorinated greenhouse gases- specifically hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur Hexafluoride (SF6)- are controlled by the Kyoto Protocol and European Union Regulations (EC) No. 517/2014. <sup>56</sup>

The <u>Kyoto Protocol</u>, also known as the Kyoto Accord, is an international treaty extends the United Nations Framework Convention on Climate Change in committing all signatories nations/state parties to internationally binding greenhouse gas emission reduction targets. The Kyoto Protocol was adopted by 84 signatories nations in Kyoto, Japan, on 11 December 1997 and entered in force on 16 February 2005. 57

<u>European Union Regulations</u>, such as (EC) No. 517/2014, also control hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF6) and aim at reducing these fluorinated gases by two thirds (2/3) from the 2014 levels by 2030. <sup>58</sup> According to the US Environmental Protection Agency (EPA), the European Union regulations for fluorinated gases (F-gas Regulations) assert the following: <sup>56</sup>

- 1. Control emissions of fluorinated gases by implementing control procedures for leak checking, proper servicing, maintenance of fluorinated gas equipment, and recovery of fluorinated gases at end of life.
- 2. Introduce prohibitions on the use of fluorinated gases if less harmful alternatives are available.
- 3. Limit the total amount of fluorinated gases that can be sold in the European Union through phased reductions in imports.



Source: U.S. Environmental Protection Agency (EPA)- *Overview of Greenhouse Gases* <sup>29</sup> https://www.epa.gov/ghgemissions/overview-greenhouse-gases



#### **Radiocarbon Dating:**

The chemical structure of renewable diesel (RD) is very similar to that of petroleum diesel. <sup>9</sup> Both fuels are mainly comprised of paraffinic hydrocarbons, also called alkanes. Therefore, it can become difficult to distinguish one from the other due to their chemical similarities. However, since renewable diesel (RD) is produced from current renewable sources, it contains of close to 100% modern/biogenic carbon, while petroleum diesel from prehistoric fossils should have none because of it is produced from ancient sources. Keeping this in mind, a reliable method for differentiating these two fuels, renewable diesel from petroleum diesel, is radiocarbon dating.

Radiocarbon dating was developed by Professor Willard Libby of the University of Chicago in the 1940's. Because of his work, Professor Libby was awarded the Nobel Prize in chemistry in 1960. <sup>59</sup> Professor Libby was inspired by the earlier work of Professor Serge Korff of New York University, who discovered that neutrons are being continuously produced during the bombardment of galactic cosmic rays in the upper atmosphere. These neutrons then collide with nitrogen-14 (<sup>14</sup>N), which is the most abundant nitrogen isotope in the atmosphere. [Isotopes of an element have the same number of protons (positive charged) but different number of neutrons (no electric charge) in the nucleus. For example, carbon has three (3) isotopes; those are <sup>12</sup>C, <sup>13</sup>C and <sup>14</sup>C. Isotopes <sup>12</sup>C and <sup>13</sup>C are stable, while <sup>14</sup>C is very unstable.]

During the collision with neutrons, nitrogen-14 ( $^{14}$ N) losses a proton and forms radioactive isotope carbon-14 ( $^{14}$ C) [neutron +  $^{14}$ N  $\Rightarrow$   $^{14}$ C + proton]. Radioactive carbon-14 ( $^{14}$ C) is highly reactive. It readily combines with the oxygen ( $O_2$ ) in the atmosphere to form carbon monoxide ( $^{14}$ CO), and eventually carbon dioxide ( $^{14}$ CO<sub>2</sub>). Over time carbon-14 decays to form nitrogen-14 ( $^{14}$ N).

Professor Libby recognized that the carbon dioxide ( $^{14}CO_2$ ) would be dispersed in atmosphere, mixed with other atmospheric gases, and eventually, it would be taken up together with the other, more stable carbon isotopes carbon-13 ( $^{13}C$ ) and carbon-12 ( $^{12}C$ ) by plants during the photosynthesis process or dissolved in the oceans. As animals (including human beings) eat the plants, they absorb radiocarbon  $^{14}C$ . Professor Libby postulated:

"We assimilate cosmic-ray produced carbon-14 atoms at just the rate that the carbon-14 atoms in our bodies disappear to form nitrogen-14. At the time of death, however, the assimilation process stops abruptly. There is no longer any process by which the carbon-14 from the atmosphere can enter our bodies." <sup>59</sup>

Based on this, Professor Libby proposed that organic matter, such as in animals or plants, while it is alive, is in equilibrium with their surroundings and stated:

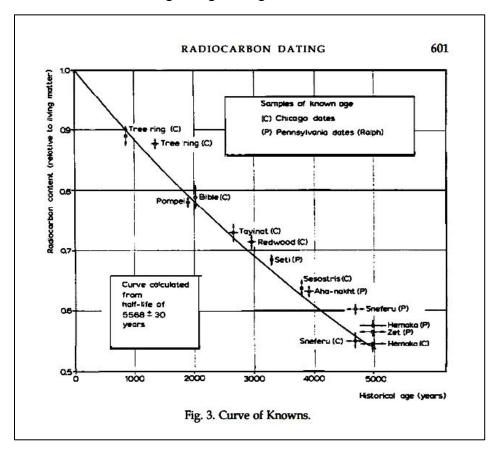
"...organic matter, while it is alive, is in equilibrium with the cosmic radiation; that is, all the radiocarbon atoms which disintegrate in our bodies are replaced by the carbon-14 contained in the food we eat, so that while we are alive we are part of a great pool which contains the cosmic-ray produced radiocarbon." <sup>59</sup>

Therefore, organic matter, while alive, have the same ratio of carbon-14 (<sup>14</sup>C) to carbon-12 (<sup>12</sup>C) as the atmosphere. Libby assumed (which was later verified to be virtually true) that the intensity of the cosmic radiation had remained constant for thousands of years, and, consequently, the amount of carbon-14 (<sup>14</sup>C) in the atmosphere, and in the plants and animals, had also remained constant over time. In addition, further research by Libby and others established the half-life, which is the of time it takes for one-half of a radioactive isotope to decay according to the law of radioactive decay, of the carbon-14 (<sup>14</sup>C) isotope to be about 5,600 years- the half-life of the carbon-14 (<sup>14</sup>C) was later revised to be 5,730 +/- 40 years. <sup>59</sup> 60



Upon death, however, the plant/animal ceases to take in carbon-14 (<sup>14</sup>C). The radioactive decay of carbon-14 (<sup>14</sup>C) to nitrogen-14 (<sup>14</sup>N) takes over within its biological matter, and eventually all carbon 14 (<sup>14</sup>C) in the dead object disappears completely. Professor Libby concluded that the age of an object can be determined if the amount of carbon-14 (<sup>14</sup>C) in that object is known. <sup>59</sup> 60

To prove his theory, Professor Libby established the age of historical artifacts whose age was already known, such as mummies and ancient Egyptian artifacts, using radiocarbon dating and compared his results with the known ages of the samples in the "Curve of Knowns" (Fig 3 on Libby's Radiocarbon dating- Noble Lecture on December 12, 1960 59) below. The comparison showed that Libby's results on the ages of the artifacts were within a small statistical error range from the known ages of the artifacts samples, which proved Libby's radiocarbon dating to be reliable method for determining the age of organic matter.



Nobel Price Organization- *Radio Carbon Dating, Nobel Lecture, December 12, 1960* 59 <a href="https://assets.nobelprize.org/uploads/2018/06/libby-lecture.pdf">https://assets.nobelprize.org/uploads/2018/06/libby-lecture.pdf</a>

The introduction of radiocarbon dating by Professor Libby revolutionized the methods of dating in various fields, particularly in archeology and geology. Today, subsequent modern advances in the detection of carbon-14 (<sup>14</sup>C) in organic matter make possible the use radiocarbon dating to accurately date up to 50,000-year-old materials.

Radiocarbon dating has become the standard test method used in industry to differentiate renewable diesel (produced from modern renewable sources) from fossil-based petroleum diesel, which has zero percent modern carbon. In the United States, radiocarbon testing is performed in accordance with the American Society for



Testing and Materials (ASTM) <u>D6866 standard-Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis</u>. 61

<u>ASTM D6866</u> identifies the carbon-14 (<sup>14</sup>C) measured as "percent modern carbon (pMC)." Zero pMC represents the complete absence of carbon-14 (<sup>14</sup>C) in the measured sample, which indicates that the sample was derived from ancient/fossil sources. Conversely, a 100 pMC denotes that the sample was produced in its entirety from modern carbon, carbon-14 (<sup>14</sup>C), sources. The pMC values must be then divided by an "atmospheric correction factor (REF)" to obtain the true biobased, or biogenic, carbon content of the sample. Test results are reported in "% biobased carbon content" or "% biogenic carbon content." 61

The main difference between biobased and biogenic % carbon contents is that biobased calculations take into account organic carbons only, whereas % biogenic carbon content are based on both organic and inorganic carbons. Organic carbon compounds have at least one carbon-hydrogen (C-H) bond, such a methane (CH<sub>4</sub>) and carbohydrates (glucose- C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>). On the other hand, inorganic carbon compounds do not have carbon-hydrogen (C-H) bonds anywhere, i.e. carbon dioxide (CO2) and carbon monoxide (CO).

Biobased carbon content is the amount of organic carbon from modern/renewable sources, such as plants and animals, in the sample as a percent of the total organic carbon (TOC) in the sample. Whereas, biogenic carbon content is the amount of organic and inorganic carbon from renewable sources like plants and animals in the product as a percent of the total carbon (TC) in the product. 61

The City of New York will be using "% biogenic carbon content" test results obtained from field samples to assure deliveries of renewable diesel (RD) to the City's municipal fuel storage sites. Lab results reporting to 100% biogenic carbon would indicate that the fuel delivered was produced from modern/renewable sources, i.e., plants and/or animals. On the other hand, a zero% biogenic carbon content signifies that the fuel sample was completely produced from fossil sources. In addition, % biogenic carbon content with values between 0% and 100% would indicate a sample containing combined proportions of carbon derived from fossil and modern/renewable sources.



#### RENEWABLE DIESEL

### **General Information:**

Renewable diesel (RD) is an advanced and sustainable biofuel produced from 100% bio-based renewable feedstocks (such as vegetable oils, animal fats, organic waste, woody biomass and algae) and whose chemical structure is very similar to that of petroleum (fossil) diesel. Renewable diesel (RD) is primarily composed of hydrocarbons. It is free of esters and has near zero aromatics, oxygen, and sulfur contents. As a result, renewable diesel (RD) delivers up to 90% reduction in greenhouse gas (GHG) lifecycle emissions when compared to petroleum diesel. 9, 10, 11

Renewable diesel (RD) goes by various names, such as green diesel, renewable hydrocarbon diesel, hydrotreated vegetable oil (HVO), hydrogenation derived renewable diesel (HDRD), Fischer-Tropsch renewable diesel (FTRD), and non-ester renewable diesel. Some of the names describe the process utilized in producing the RD fuel, whereas other names refer to its chemical components.

Renewable diesel (RD) is not biodiesel. There are three (3) main differences between the two (2) biofuels:

- I. Renewable diesel (RD) can be produced from the same renewable feedstocks as biodiesel, i.e., vegetable oils, animal fats, grease and algae. However, RD can also be produced from cellulosic biomass- such as wood biomass and crop residues- unlike biodiesel. <sup>9</sup>
- II. The production processes for biodiesel and renewable diesel (RD) are very different. Biodiesel is produced exclusively through a transesterification process, which is a process where vegetable oils and/or animal fats are reacted with short-chain alcohol in the presence of a strong catalyst to form methyl ester of fatty acids-i.e., fatty acid methyl ester (FAME) in biodiesel. <sup>9</sup>

On the other hand, renewable diesel (RD) can be produced via numerous thermochemical processes, including:  $\frac{9,62}{}$ 

- *Hydrogenation (hydrotreating) of fats/oils/esters*
- Co-processing with petroleum oil in a refinery
- Biomass pyrolysis (liquification of biomass)
- Catalytic conversion of sugars (from carbohydrates into hydrocarbon fuels)
- Biomass-to-liquids (Fischer-Tropsch (FT) gasification)
- Biogas-to-liquids (GTL)
- III. Renewable diesel (RD) is chemically very similar to petroleum diesel in that it is composed of straight-chain hydrocarbons. RD is generally indistinguishable from petroleum diesel and has many alike properties as both fuels adhere to the same ASTM International specification, <u>ASTM D975- Standard Specification for Diesel Fuel Oils</u>. Contrastingly, biodiesel is comprised of fatty acid methyl esters (FAME), which are branched molecules, resulting in notable differences in the physical properties of biodiesel (ASTM D6751) when compared to diesel (ASTM D975).



The U.S. Department of Energy (DOE) defines renewable diesel (RD) as "a biomass-derived transportation fuel suitable for use in diesel engines. It meets the <u>ASTM D975</u> specification in the United States and EN 590 in Europe." <sup>9</sup> Current literature have shown that renewable diesel (RD) not only meets all critical requirements of <u>ASTM D975</u> but outperforms petroleum diesel in some of them, such as the Cetane Index value, while delivering cleaner combustion and significant reductions in greenhouse gas (GHG) lifecycle emissions and other types of emissions, i.e., particulate matter (PM). nitrogen oxides (NOx), and carbon monoxide (CO). <sup>9, 10, 11, 61</sup>

While DOE limits its definition of renewable diesel (RD) to the transportation sector as biofuel meeting <u>ASTM</u> <u>D975</u>, both the Internal Revenue Service (IRS) and the U.S. Department of Agriculture (USDA) expanded their classification to include the use of renewable diesel (RD) as heating fuel.

The Internal Revenue Service (IRS) in its <u>Internal Revenue Bulletin: 2007-17 dated June 23, 2007, Section 2.</u>

<u>RENEWABLE DIESEL; RENEWABLE DIESEL MIXTURE</u> defines renewable diesel (RD) as a biomassderived diesel fuel that "*Meets the requirements of the American Society of Testing and Materials (ASTM) <u>D975</u>

or <u>D396</u>." Thus, the IRS includes <u>ASTM D396</u>, which is the Standard Specification for Fuel Oils, in its
definition of renewable diesel (RD).* 

The U.S. Department of Agriculture (USDA) also requires that renewable diesel (RD) meet the <u>ASTM D396</u> for heating oil, and in its July 13, 2016 presentation "<u>Biofuel in Diesel and Heating Oil</u>," § states "*Renewable diesel can be used in any proportion in diesel or heating oil*." §

# **Renewable Diesel (RD) Properties:**

Because the chemical structure of renewable diesel (RD) is very similar to that of petroleum diesel, RD meets the specifications set forth on ASTM standards <u>ASTM D975- Standard Specification for Diesel Fuel Oils</u> and <u>D396- Standard Specification for Fuel Oils</u>.

Since renewable diesel (RD) is essentially composed of hydrocarbons, it has a lower density than that of conventional diesel, which contains aromatics, oxygen and sulfur among other components. The density of renewable diesel (RD) at 59°F has been reported between 775 and 785 kg/m³, whereas that of diesel fuel is about 835 kg/m³. 65

The heating value (calorific value), which is the amount of heat released when an specific quantity of the fuel is combusted, by volume of renewable diesel (RD) is about 34.4 MJ/l, while diesel has a heating value around 35.7 MJ/l. Hence, RD's heating value by volume is around 4% lower than that of diesel. However, the heating value by mass is higher for RD than for diesel,  $\sim$  44.0 MJ/kg versus  $\sim$ 42.7 MJ/kg. As a note, biodiesel's heating value by volume is about 33.2 MJ/l or  $\sim$ 7% below that of diesel.  $^{65}$ 

Carbon intensity (CI), which is the amount by weight of carbon emitted per unit of energy consumed, is measured in grams of carbon dioxide equivalent per megajoule (gCO2e/MJ). According to the <u>U.S. Energy Information Administration (EIA)</u>, renewable diesel (RD) has an average lifecycle CI of 30 gCO2e/MJ, which is about equal to that of biodiesel. For comparison, ultra-low sulfur diesel (ULSD) has a CI of about 102 gCO2e/MJ. This means that renewable diesel (RD) releases on average 70% less carbon emissions during its lifecycle than ULSD. 66



As per the <u>California Air Resources Board's (CARB's) Low Carbon Fuel Standards Pathways Certified Carbon Intensities</u> webpage, <sup>12</sup> depending on the feedstock and production process, the individual lifecycle carbon intensity (CI) for renewable diesel (RD) ranges from 16.89 gCO2e/MJ to 51.90 gCO2e/MJ. This is excluding Fischer-Tropsch Diesel (FTD) from organic waste from Fulcrum Sierra BioFuels that has a CARB certified lifecycle pathway CI of 14.78 gCO2e/MJ. <sup>12</sup>

Another important property of renewable diesel (RD) is that it is fully fungible and compatible with diesel. Unlike biodiesel, renewable diesel (RD) can be co-processed in the same refineries with diesel and distributed using the existing diesel pipelines. Renewable diesel (RD) follows the same logistics as ultra-low sulfur diesel (ULSD). Consequently, RD goes from production to storage to distribution through the same diesel infrastructure.

In addition, since renewable diesel (RD) contains no oxygen, it can be stored for long periods without experiencing water accumulation or any microbial growth deterioration.

Currently, renewable diesel (RD) manufacturers, such as Neste <sup>10</sup> and the Renewable Energy Group (REG), <sup>11</sup> produce RD fuel through the process of hydrogenation using designed specifications so that the final RD products meet the ASTM D975 and D396 standards. Neste and the Renewable Energy Group (REG) published the general properties of their RD fuels. <sup>10</sup>, <sup>11</sup>

In 2011, the California Air Resource Board (CARB) conducted a study on the characterization of biodiesel that also covered Neste's NExBTL renewable diesel (RD), "Biodiesel Characterization and NOx Mitigation." <sup>63</sup> The study's final report included the NExBTL's properties as analyzed by CARB. <sup>63</sup>

More recently, in 2018, the Department of Citywide Administrative Services (DCAS) of the City of New York successfully conducted a pilot with one million gallons of Hydrogenation Derived Renewable Diesel (HDRD) that fueled municipal vehicles from the New York City's fleet from June 3, 2018 to October 31, 2018. The pilot included lab sample testing of the HDRD deliveries, and the average test results were documented on the final report. <sup>64</sup>

Table 1, *Renewable Diesel Reported Properties and Test Results in Comparison to ASTM Standards D975-18 and D396-18*, below presents the properties of renewable diesel (RD) as reported by NYC DCAS, <sup>64</sup> Neste, <sup>10</sup> REG <sup>11</sup> and CARB. <sup>63</sup> In all cases the renewable diesel fuels met both ASTM standards, <u>ASTM D975- Standard Specification for Diesel Fuel Oils</u> and D396- Standard Specification for Fuel Oils.



Table 1- Renewable Diesel (RD) Reported Properties/Test Results in Comparison to ASTM Standards D975-18 and D396-18

		Reported RD Propert	ASTM Standards ****			
Test Method Property	NYC DCAS RD (Non-winterized) Pilot- Average Test Results	Neste Renewable  Diesel  Reported*	California Air Resources Board (CARB)- NExBTL Test Results**	Renewable Energy Group (REG) Reported***	ASTM D975-18 2DULS Spec	ASTM D396-18 2DULS Spec
ASTM D86 Distillation Temperature, 90% Recovery	574.5 °F	540°F to 640°F	547 °F	540°F to 640°F	540°F to 640°F	540°F to 640°F
ASTM D93 Flash Point	158 °F	>142 °F	146 °F	126°F Minimum	126°F Minimum	101°F Minimum
ASTM D130 Copper Corrosion @122°F/3hr	1a	No. 1	1a	No. 1	No. 3 Maximum	No. 3 Maximum
ASTM D445 Kinematic Viscosity @104 °F	3.358 cSt	2.00 cSt to 4.00 cSt	2.5 cSt	1.9 cSt to 4.1 cSt	1.9 cSt to 4.1 cSt	1.9 cSt to 4.1 cSt
ASTM D482 Ash, mass %	<0.001 mass %	<0.001 mass %	<0.001 mass %	0.01 mass %	0.01 mass % Maximum	(No spec for 2DULS)
ASTM D2500 Cloud Point	9.1°F (ASTM D5773 Automatic Cloud Point)	As needed from -29°F to 23°F	-17 °F	Report	As provided in Appendix X5 of the ASTM D975 standard	(No Spec)
ASTM D97 Pour Point	(Not reported)	(Not reported)	-53 °F	(Not reported)	(No Spec)	21 °F Maximum
ASTM D2709 Sediment and Water	<0.01 volume %	<0.02 Volume %	<0.2 mL (ASTM D1796)	0.05 volume %	0.05 Vol.%	0.05 Vol. %
ASTM D524 Ramsbottom Carbon Residue on 10% distillation Residue	0.05 mass %	<0.10 mass %	<0.02 mass %	0.35 mass %	0.35 mass % Maximum	0.35 mass % Maximum
ASTM D5453 Sulfur Content	<1.0 ppm	<5.0 ppm	0.3 ppm	2 ppm	15 ppm Maximum	15 ppm Maximum
ASTM D6079 Lubricity, HFRR at 140 °F (Wear Scar Diameter)	401 μm	≤460 μm	(Not reported)	(Not reported)	520 μm Maximum	520 μm Maximum
ASTM Cetane Number or Cetane Index	94.8 (Cetane Index- ASTM D4737 Procedure A)	>70.0 ( Cetane Number)	72.3 (Cetane Number- ASTM D613-94)	65 minimum (Cetane Number- ASTM D613)	40 Minimum (Cetane Number- ASTM D613)	(no spec)
ASTM API Gravity @ 60°F	<b>48.8</b> (ASTM D4052)	(Not reported)	(Not reported)	(Not reported)	(No spec)	(No spec )
EN 14078 Fatty Acid Methyl Ester (FAME) Range A	<0.05 % V/V	0 % V/V	(Not reported)	(Not reported)	(No Spec)	(No spec for 2DULS)
ASTM D1319 Aromaticity Content	<5.0 Vol%	<1.0 mass %	0.4 mass % (ASTM D5186-96)	2 volume %	35 Vol% Maximum	(No spec)
ASTM D1298 Density at 59 °F	(Not reported)	770-790 kg/m <sup>3</sup>	(Not reported)	(Not reported)	(No spec)	876 kg/m <sup>3</sup> Maximum
ASTM D2624/D4308 Conductivity (pS/m)	(Not reported)	50 pS/m minimum	135 pS/m (ASTM D2624)	25 pS/m minimum	25 pS/m minimum	25 pS/m minimum
ASTM D6866 % Biogenic Carbon as a fraction of total carbon	99%	Not reported	(Not reported)	(Not reported)	(No spec)	(No spec)
	DCAS Report- Demonstration on Renewable Hydrocarbon Diesel (2019) (A copy is included in this report)	*) Neste Reneable Diesel Handbook (https://www.neste.com/si tes/neste.com/files/attach ments/neste renewable d iesel_handbook.pdf)	**) CARB- "Biodiesel Characterization and NOx Mitigation Study" October 2011 (https://ww3.arh.ca.gov/fuels/diesel/altdiesel/2011 013_carb%20final%20biodiesel%20report.pdf)	***) Renewable Energy Group (REG) (https://www.regi.com/docs/ default-source/factsheets/reg- 19029 rd factsheet 2019upda tes.pdf?sfvrsn=ac183c01_2)	****) ASTM International (https://www.astm.org/)	



#### **Renewable Diesel (RD) Benefits:**

Renewable diesel (RD) is an advanced hydrocarbon-based and drop-in alternative fuel with chemical structure very similar to that of petroleum diesel. Because of this, RD is fully fungible with petroleum diesel and compatible with all diesel engines and all existing diesel distribution infrastructures without modifications. <sup>10</sup>, <sup>11</sup>, <sup>62</sup>

Additionally, renewable diesel (RD) can used as a direct, straight forward replacement for diesel in its pure form (RD100) or blended with diesel and/or biodiesel. RD adheres to the same biodiesel blend limitations as regular diesel. However, RD has no blend wall with diesel, and it can be readily blended with conventional diesel at all blend levels, up to 100%.

Renewable diesel (RD) is produced from 100% renewable, sustainable, modern feedstocks, including the same feedstocks as biodiesel: <sup>9</sup>

- Animal fats,
- cooking grease,
- vegetable oils,
- algae,
- crop residues,
- organic waste,
- and woody biomass.

Palm oil can also be used as a source in the production of renewable diesel (RD). However, there are serious environmental concerns with the use of palm oil as biofuel feedstock since palm oil production is considered one of the key drivers of the deforestation and destruction of land, swamps and precious rainforests in Southeast Asia and South America. The destruction of natural habitats to create massive palm plantations increases greenhouse gas (GHG) emissions, which in turn leads to global warming. As a result, the lifecycle carbon emissions of renewable diesel (RD) from palm oil exceed that of petroleum diesel. <sup>68</sup> For these reasons, many scientists and environmental experts agree that at the present time, renewable diesel (RD) from palm oil does not offer any lifecycle environmental benefits when it is used instead of petroleum diesel. <sup>68</sup>, <sup>71</sup>, <sup>72</sup>

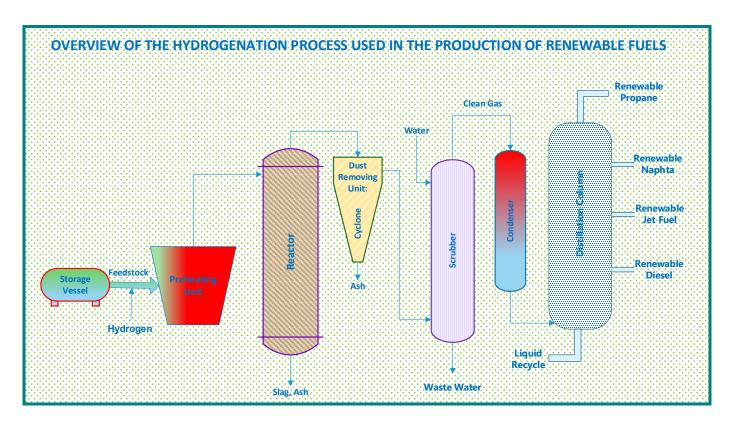
Renewable Diesel (RD) is a clear and odorless fuel that is virtually free of fossil carbons, sulphur, oxygen, metals, and aromatics. It burns more efficiently/cleaner than petroleum diesel, and it has a higher heating value (per mass and per volume basis) than biodiesel. RD has excellent cold flow properties and storage stability with no storage issues, such as microbial growth or water contamination. 10, 62

Renewable diesel (RD) can be produced using various thermochemical processes, which include: 9,62

- *Hydrogenation (hydrotreating) of fats/oils/esters*
- Co-processing with petroleum oil in a refinery
- Biomass pyrolysis (liquification of biomass)
- Catalytic conversion of sugars (from carbohydrates into hydrocarbon fuels)
- Biomass-to-liquids (Fischer-Tropsch (FT) gasification)
- Biogas-to-liquids (GTL)

Presently, renewable diesel (RD) is typically produced through hydrotreatment of animal or vegetable fats at a biorefinery, or it is being co-processed at a petroleum refinery.





Most importantly, considering its impact on the environment, renewable diesel can significantly reduce harmful emissions, such as greenhouse gas (GHG), hydrocarbon, and carbon monoxide (CO) emissions when it is used instead of petroleum diesel.

Many cities in the State of California, such as San Francisco, Oakland, Sacramento and San Diego, have switched their municipal fleets to renewable diesel (RD) to fuel their city vehicles, including heavy-duty trucks and buses, because of the carbon emission reduction benefits that RD's offers. For example, the Metropolitan Transportation Agency of San Francisco reported a reduction of 10,000 tons of carbon dioxide (CO<sub>2</sub>) when 632 of their transit buses used renewable diesel (RD) for a year. <sup>69</sup>

In addition, in the State of Oregon several fleets use renewable diesel, including the City of Portland, the City of Corvallis, and the City of Eugene Water & Electric Board. And, a number of private companies, such as UPS and Google, have also transitioned their fleets to renewable diesel (RD) without experiencing any issues.

The <u>California Air Resources Board's (CARB's) Low Carbon Fuel Standards Pathways Certified Carbon Intensities</u> certified pathways for renewable diesel (RD) with carbon intensities (CIs) of up to 85% lower than that of conventional diesel. This means that renewable diesel can reduce by up to 85% of the lifecycle greenhouse gas (GHG) emissions when compared to petroleum diesel. <sup>12</sup>

Additionally, the substitution of conventional diesel with renewable diesel (RD) results in significant reductions of harmful emissions. Renewable diesel (RD) manufacturers Neste <sup>10</sup> and the Renewable Energy Group (REG) <sup>11</sup> reported the following percent reductions for their RD product compared to petroleum diesel:



PERCENT EMISSION REDUCTIONS OF 100% RENEWABLE DIESEL (RD) COMPARED TO PETROLEUM DIESEL						
Pollutant	Renewable Energy Group (REG) 11	Neste 10				
Particulate Matter (PM)	$\sim 40\%$	33%				
Nitrous Oxide (NOx)	15%	9%				
Carbon Monoxide (CO)	More than 25%	24%				
Total Hydrocarbons (THC) Or Hydrocarbons (HC)	More than 10% (THC)	30% (HC)				

The City of New York is also looking at using Renewable diesel (RD) to fuel its municipal fleet in its effort to achieve 80% greenhouse gas (GHG) emission reduction from the 2005 GHG emission levels by 2050 (80X50). <sup>3</sup> To that end, in the summer of 2018, the City successfully conducted a demonstration pilot with nearly one million gallons of renewable diesel (RD) that fueled city vehicles across many agencies. <sup>64</sup> Based on the success of the demonstration, the City of New York is in the process of bidding/implementing a long-term contract for the purchase of renewable diesel (RD) for its municipal fleet.

But beyond that, the City of New York is exploring the groundbreaking implementation of using renewable diesel (RD) as the heating fuel for its municipal buildings. According to the "*Inventory of New York City Greenhouse Gas Emissions in 2016*," which was published by the City of New York in December of 2017, stationary energy use in buildings is the largest source of GHG emissions in the City. <sup>5</sup>

Using renewable diesel (RD) as heating fuel could reduce the GHG emissions from municipal buildings by as much of 85% in accordance with the <u>California Air Resources Board's (CARB's) Low Carbon Fuel Standards Pathways Certified Carbon Intensities.</u> 12

Presently, there are no known technical concerns/issues with replacing diesel oil with renewable diesel (RD) as the heating fuel for buildings. R. W. Beckett, which is one of the largest domestic manufacturer of oil burners used in the Oil Heat Industry, evaluated renewable diesel (RD) as heating oil for their burners and were very pleased with their experience. Because renewable diesel (RD) offers many advantages over biodiesel, such as having better storage stability and cold flow properties, R.W. Beckett would like to promote the use of renewable diesel in the Oil Heat Industry. <sup>70</sup>

The City of New York anticipates to successfully conduct a pilot using renewable diesel (RD) as heating fuel for various municipal buildings. Subsequently, the City plans to go out to bid and implement a long-term contract to purchase renewable diesel (RD) as heating fuel for its city buildings.



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