The Next Generation of BIOFUELS for the U.S. Military

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The United States Department of Defense is committed to reducing its petroleum energy consumption in an effort to decrease its reliance on foreign oil and the volatile markets that supply it. Title 10 of the USC, § 2911 dictates that the DoD obtain no less than 25 percent of the total energy it consumes within its facilities from renewable sources by the year 2025, and every year thereafter.

Renewable energy sources, such as wind and solar power, provide an excellent opportunity to reduce petroleum consumption at permanent installations; however, other energy sources and/or storage systems are necessary due to the inconsistent energy production of wind and solar power. Furthermore, land and air vehicles, forward deployed military installations, ocean going vessels and other non-stationary military facilities are large consumers of petroleum-based energy that cannot currently be substantially displaced by wind or solar power. Thus, alternatives to petroleum based fuels, such as F-76, JP8 and other compression ignition or jet fuels are essential to reducing the DoD's petroleum consumption.

Biodiesel, as defined by the American Society of Testing and Materials, is a "fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats." [1] Biodiesel, herein, refers to a biofuel suitable for CI engines produced by the primary process of transesterification. The manufacture of biodiesel through transesterification begins with feedstocks containing lipids, such as fats, oils and greases. Recycled and virgin vegetable oils and animal fats are the predominant feedstocks; however, other biological matter composed predominantly of triglycerides may also be suitable for biodiesel production via transesterification. [2]

Through transesterification, triglycerides are chemically reacted with an alcohol, typically methanol or ethanol, to produce esters and glycerol. [3] Esters, namely fatty acid methyl esters, are the resulting biodiesel while glycerol is a byproduct of the reaction. The transesterification process is an equilibrium reaction that can occur fundamentally by mixing the reactants; howev-

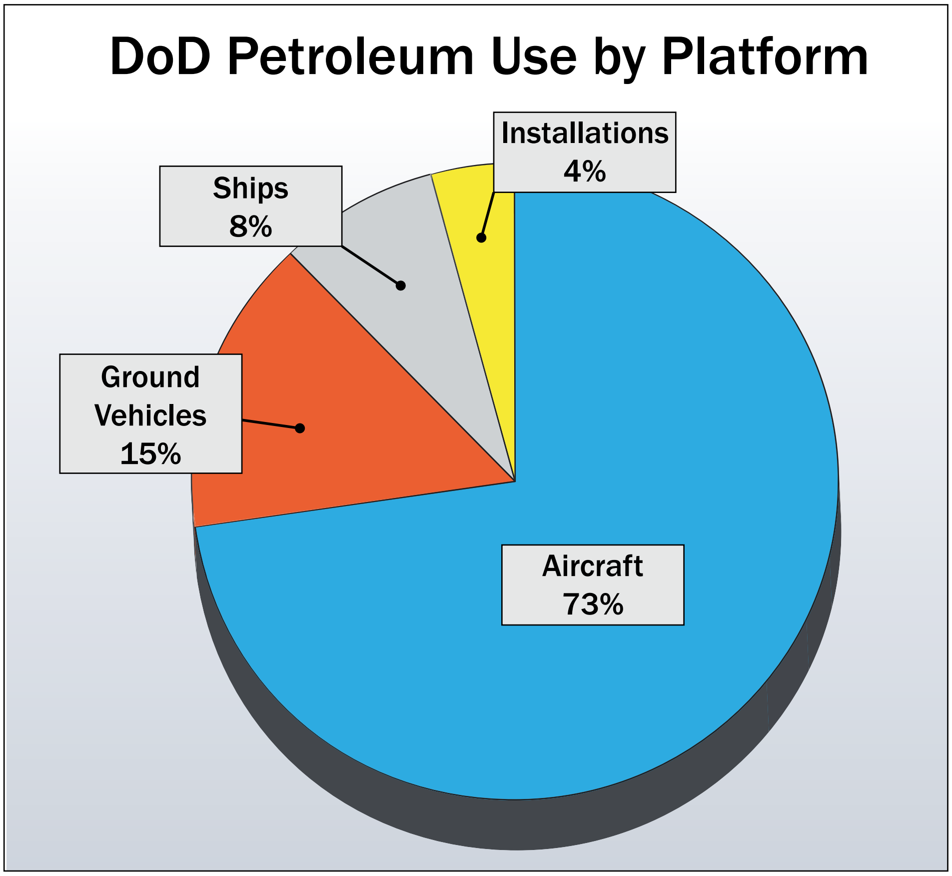

Figure 1: DoD petroleum use by platform. (Released) [7]

er, the use of a catalyst, most commonly a strong base such as sodium or potassium hydroxide, is used to accelerate the reaction. [3] The alcohol must be used in excess (approximately 1.6 times the stoichiometric concentration) to ensure a complete reaction, and the reaction can be hindered by other components in the feedstock, such as water and free fatty acids. [4] Thus, prior refinement of the feedstock is necessary for increased yields of FAME suitable for use as a fuel. The FAME can be separated from the glycerol and other byproducts because of the low solubility of glycerol; however, the crude glycerol stream is only approximately 50 percent glycerol and contains excess alcohol, most of the catalyst and soap, which must be removed prior to sale as industrial glycerol. [4]

FAME-based biodiesel, otherwise known as conventional biodiesel, produced by this process is most often used in a form blended with petroleum-derived diesel designated B5, B20 and B100, for example, which describes the ratio of biodiesel to petroleum diesel. It can be used in neat form depending on the application; however, conventional biodiesel has several significant differences from petroleum diesel that complicate its neat use, transport and storage characteristics, as well as its application as a jet fuel.

One such difference is conventional biodiesel contains a modest amount of oxygen, on the order of 10 percent, [5] while petroleum-based diesel contains no oxygen. While this oxygen content can improve soot, carbon monoxide and hydrocarbon exhaust emissions, it detracts from the energy content of the fuel, and possibly even more concerning, it can encourage microbial growth during storage. Furthermore, trace amounts of glycerine remaining in the fuel can form sediment that may plug filters and small passageways. [6] Another concern is the higher cloud point of conventional biodiesel versus petroleum diesel, which makes it more susceptible to gelling and cold flow problems.

These properties of biodiesel make it unsuitable for use as a jet fuel, which is relevant when considering alternative fuels for military applications and the fact that, "when divided by platform type, aircraft are the DoD's largest users of petroleum. According to a 2006 Navy report, in 2003 aircraft accounted for 73% of DoD's petroleum use, ground vehicles accounted for 15%, while ships accounted for 8%. DoD installations accounted for 4%," which is displayed in Figure 1. [7] Due to the incompatibility of biodiesel as a jet fuel, special precautions must be taken during transport and storage to ensure that traces of it do not mix with and potentially contaminate jet fuel, which is a valid concern when diesel and jet fuel share the same transport means or storage tanks.

The next, or second, generation of biofuels for reciprocating CI engines have overcome many of the challenges found with first generation bio fuels (i.e., conventional biodiesel produced by transesterification). One such next generation biofuel is hydroprocessed renewable diesel, often called green diesel or, simply, renewable diesel. This fuel can be produced from all the same feedstocks as conventional biodiesel in addition to others not suitable for the transesterification process. The hydrogenation procedure used to produce HRD easily converts free fatty acids to paraffins, unlike conventional biodiesel production via transesterification for which they can limit the reaction and react with the base catalysts to produce soaps. [6] Furthermore, the hydrogenation process is already in use by petroleum refineries to remove sulfur and other contaminants from petroleum.

Therefore, much of the infrastructure and technology to mass produce this fuel exists and is currently commercially available. The process can also be used to produce hydroprocessed renewable jet fuel suitable for aircraft. The chemical composition of HRD and HRJ is composed wholly of paraffinic hydrocarbons and contains minimal to no olefins, aromatics, naphthenes or oxygen. [8] As such, HRD and HRJ fuels resemble petroleum-based diesel and jet fuels much more than conventional biodiesel, which minimizes storage challenges, compatibility with seals and other fuel system materials, as well as viscosity and cloud point concerns.

While the hydrogenation process is fundamentally the same, there are several variations to the process depending on the feedstock used. As noted, biomass containing substantial components other than triglycerides can be converted to HRD or HRJ with this process, but the level of pretreatment required may increase to ensure the effectiveness of the hydroprocessing catalysts. [6] With regard to vegetable oil, animal fats and other bio-matter comprised predominantly of triglycerides, the process begins with one of two processes, hydrodeoxygenation or decarboxylation to remove oxygen from the triglycerides and form long chain n-paraffins. Both of these processes are performed with the addition of hydrogen and typically some form of a nickel- or cobalt-molybdenum catalyst. [6]

However, the amount of hydrogen required and the byproducts vary depending on the process as well as the feedstock. For example, beginning with rapeseed oil, the hydrodeoxygenation reaction requires 16 moles of hydrogen, produces 1 mole of propane and 6 moles of water, while decarboxylation requires 7 moles of hydrogen, produces 1 mole of propane and 3 moles of carbon dioxide. [6] Note that depending on level of reverse water gas shift reaction and methanation in the decarboxylation process, the required moles of hydrogen can increase to 16. After separation processes, the paraffinic products can be distilled to provide a fuel with similar distillation temperatures as petroleum diesel, high cetane number, but typically poor cold flow or cloud point properties. This fuel and the remaining heavier hydrocarbons can be further refined by hydroisomerization to tailor the cold flow properties of the fuel, effectively converting n-paraffins to iso-paraffins, [9] which is particularly useful for the manufacture of HRJ fuel to be blended with petroleum jet fuel. Figure 2 provides a general comparison of the production processes involved with conventional biodiesel versus HRD fuel.

HRD and HRJ fuel produced by the previously described hydrogenation process exhibit several advantageous properties in comparison to petroleum-based fuel and conventional biodiesel. Notably, these fuels do not contain oxygen and therefore do not share the same concerns with microbial growth and oxidative stability that plagues conventional biodiesel. To the contrary, the absence of oxygen does not provide the soot, hydrocarbon and carbon monoxide oxidation benefits offered by biodiesel; however, the wholly paraffinic chemical composition of HRD offers potential reductions in soot compared to petroleum diesel due to the absence of significant heavy soot forming compounds, such as aromatics and a lower carbon intensity. HRD exhibits a relatively high cetane number, or CN, (70 to 90) when compared to biodiesel (45 to 55) and petroleum-based number 2 diesel (40 to 45). [5]

This high CN can provide improved cold-start ability and performance benefits if engine control is tailored to the fuel properties. Among the three fuels discussed, HRD typically exhibits the highest energy content by mass, slightly higher than petroleum diesel due to the paraffinic composition, and modestly higher than biodiesel mainly due to the lack of oxygen. The cold flow and cloud point characteristics of HRD are much better suited for cold climates when compared to biodiesel and can be tailored to the application via hydroisomerization, which is critical for jet fuel applications and to be an approved DoD fuel.

The use of HRD and HRJ fuel provides the U.S. military with a bio-derived fuel to offset the consumption of petroleum-based diesel and jet fuel. The feedstocks for these renewable fuels can be produced domestically and refined domestically limiting foreign oil dependence petroleum market volatility while helping to achieve renewable energy goals. In fact, trials with HRD and HRJ have already been completed by the U.S. Navy, Army and Air Force.

The Navy's Great Green Fleet is a prime example, a carrier strike group for which the carrier operates on nuclear power while its escort ships utilize a blend of HRD produced from beef tallow and petroleum diesel. [10] Currently, this blend is only 10 percent HRD and 90 percent petroleum diesel; however, the blend is cost competitive with traditional fuels and is considered a "drop in" replacement. [11]

Tests and trials have been performed with neat HRD or HRJ fuels by other groups in the U.S. military. The U.S. Army's Tank Automotive Research, Development and Engineering Center evaluated HRD fuel in a Caterpillar C7 at the TARDEC Fuels and Lubricants Research Facility. [12] The engine was exercised over the 210-hour tactical wheeled vehicle cycle for a total of 840 hours at ambient conditions and 840 hours at desert conditions. Regardless of the environmental conditions, the author concluded that the use of HRD in the Caterpillar C7 "provides adequate performance without any negative impact on engine durability,

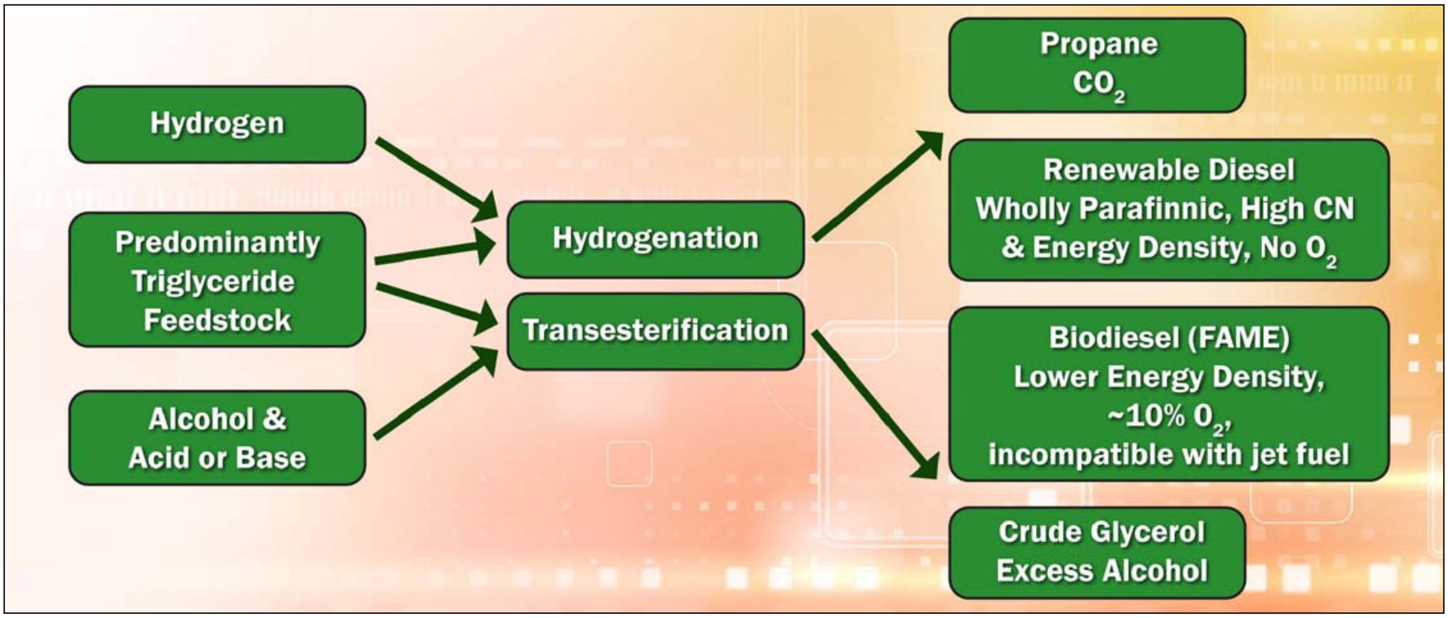

Figure 2: Overview of production processes for biodiesel and hydroprocessed renewable diesel. (Released)

emissions, performance, fuel consumption, lubricant degradation, or cleanliness." [12]

The HRD used for this study was considered neat, but it should be noted that it did contain 1.1 percent of petroleum diesel from the supplier for tax crediting purposes. With respect to jet fuel, the Air Force has certified 50 percent HRJ fuel blends with 50 percent petroleum-based jet fuel for use in its entire fleet of aircraft; however, research concerning the use of neat HRJ and other bio-based jet fuels has demonstrated issues preventing their use in neat form. [13] These issues include, "material compatibility (elastomer swelling/shrinkage), tank gauging (density), and additive compatibility (solubility)," which are likely related to the lack of aromatics in the HRJ fuel requiring the blending with petroleum-based fuel. [14]

One potential solution, to provide a 100 percent bio-derived jet fuel, has been developed by Applied Research Associates. Similar to other methods discussed, the process begins with renewable plant oils (i.e., triglycerides) but utilizes a catalytic hydrothermolysis process proceeded by a less intense hydrogenation and distillation (compared to the previously discussed HRJ fuels) that effectively converts triglycerides into "high-density aromatic, cycloparaffin, and isoparaffin hydrocarbons identical to the hydrocarbons in Jet A fuels from petroleum." [15]

With established production methods in place and continuing research on improving the yields, efficiency and quality of biofuels, next generation biofuel research is poised to focus on new feedstocks and advanced processes to exploit them. The production of first generation biofuels often directly competed with food production or indirectly through arable farm land earmarked for food production.

This was especially evident with ethanol produced from corn and biodiesel produced from soy beans. The expansion of biofuel production methods and investment in new production technologies have driven the focus toward feedstocks not involved in the production of food that have high oil outputs and can be grown on non-arable land. Animal waste feedstocks, such as beef tallow, are already in use as feedstocks for biodiesel and HRD production and do not compete directly with food production. However, the scalability to large production quantities presents a challenge.

Several non-edible feedstocks have been identified and are even in use, notably Jatropha, algae and lignocellulosic feedstocks. Regrettably, the excitement about Jatropha, once hailed as a biofuel game changer, has diminished in recent years, as researchers have noted that while Jatropha can be grown on non-arable land, it requires water and nutrients similar to other crops to be a substantial oil producer.

Furthermore, oil is produced from the seeds of Jatropha leaving the rest of the plant as waste. This has led to focus on the conversion of lignocellulosic feedstocks not substantially comprised of triglycerides such as agricultural waste or wood-based paper and pulp byproducts to oils suitable for the hydrogenation process. Prior to the use of lignocellulosic feedstocks in the hydrogenation process the cellulose, hemicellulose and lignin comprising these feedstocks must be broken down into smaller molecules with the use of technologies such as pyrolysis or by thermal or catalytic depolymerization. [6] Unfortunately, this additional process makes the use of these feedstocks less financially and environmentally appealing compared to triglyceride-based feedstocks.

Algae, considered a third, or future, generation biofuel, is an appealing feedstock that has garnered significant interest to produce not only renewable diesel, but also renewable gasoline and other valuable products. Appealing factors include algae's versatility: it can be grown in salt water, fresh water, waste water and brackish water; most species exhibit high growth rates; and many species of algae are inedible, thus it does not compete in terms of land use and food production. Furthermore, CO_2 from industrial processes and power plants can be captured and used to grow algae in addition to sunlight.

The versatility and proliferation of algae does have drawbacks, however. There are approximately 55,000 species and 100,000 strains of algae. [16] Of these, only a handful are commercially cultivated worldwide. This raises concerns of cross contamination where species not as well suited for fuel production may infiltrate a farm, potentially ruining the crop.

Nonetheless, this hurdle has led to new innovations, where semi closed algae production units have been developed, such as photo bioreactors, that allow for better utilization of CO_2, protect from invasive species and increase production yields with respect to ground space. These type of production units can stack vertically to increase yield density with respect to land use.

The conversion methods to produce biofuels from algae have also garnered significant research attention. One existing approach, hydrothermal liquefaction, is used to produce bio-oil which is a "viscous, corrosive, and unstable mixture of organic compounds." [17] This bio-oil must be further refined through other processes, such as hydrogenation, to produce renewable fuels. One advantage of this method lies in the use of wet algal biomass with little to no preprocessing; however, there are a number of high value components that are destroyed in the process.

An alternative to this process, which retains high value components, yet allows for the extraction of lipids for fuel production, is fractionation. [18] In this process, algal biomass is fractioned into carbohydrate, lipid and protein-rich components where the carbohydrates can be fermented to ethanol, the lipids can be hydroprocessed to HRD and the protein-rich compounds can be converted to biogas via anaerobic digestion for cogeneration of heat and power at the processing facility. [18]

The use of these next generation biofuels in conjunction with new engine and vehicle technologies presents a unique situation to increase fuel efficiency while further reducing petroleum based fuel consumption. A prime example can be found in the advantageous properties of HRD fuel. The high CN of the fuel makes it well suited for advanced combustion strategies that utilize high rates of dilution (exhaust gas recirculation) to limit harmful soot and oxides of nitrogen emissions while retaining high thermal efficiencies.

Furthermore, the lower carbon intensity of this wholly paraffinic fuel has the propensity to produce less soot and CO exhaust emissions during conventional combustion. Dual fuel applications, such as diesel-natural gas engines, which use the compression ignition of diesel to ignite natural gas (or other high octane number fuels), substantially benefit in terms of power density and combustion stability when a high CN fuel is used. [19] This is especially appealing for the algal fractionation approach previously discussed for which biogas and renewable diesel are both produced and could be utilized in a dual fuel engine for power generation and heat production.

Such applications could allow for solar or wind to provide base load power and the use of biofueled internal combustion engines for peak power demands. The parallel path of new technologies such as advanced fuel quantification sensors and in-cylinder pressure and temperature sensors in addition to advanced engine control technologies with these next generation biofuels present further opportunities to reduce fuel consumption. With known fuel properties or feedback on the in-cylinder combustion pressure or temperature, engine control changes such as fuel injection timing, pressure and duration can be made to exploit a particular fuel's properties and combustion characteristics to ensure maximum efficiency and minimal harmful emissions.

The role of the DoD in the evolution of bio-derived fuels is significant. Within the last decade, significant innovations have been made in the realm of bio-derived fuels. The hydroprocessing of renewable feedstocks to HRD or HRJ fuel has overcome many of the restrictions for DoD use found with the use of first generation, conventional biodiesel produced from transesterification. These second generation biofuels can be made from a wider range of feedstocks and have fuel properties much more consistent with petroleum diesel when compared to conventional biodiesel.

Furthermore, it has been proven that HRD fuel can be used in neat form for internal combustion, CI engines and new conversion processes are being refined to use HRJ fuel in neat form for aircraft. The future generation of bio-derived fuels is promising, with research targeting the efficient conversion of lignocellulosic and algae feedstocks to fuels equivalent and potentially improved performance over petroleum fuels. Merging these future bio-derived fuels with advanced engine and combustion technologies provides a promising pathway for significant reductions in petroleum usage by the DoD. ■

References

1. ASTM International. (2015). Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. West Conshohocken, Pennsylvania, USA.
2. Milbrandt, A., Kinchin, C., & McCormick, R. (2013). The Feasibility of Producing and Using Biomass-Based Diesel and Jet Fuel In the United States. Golden: National Renewable Energy Laboratory.
3. Schuchardt, U., Sercheli, R., & Vargas, R. M. (1998). Transesterification of Vegetable Oils: A Review. Journal of the Brazilian Chemcial Society, 199-210.
4. Gerpen, J. V. (2005). Biodiesel processing and production. Fuel Processing Technology, 1097– 1107.
5. Hoekman, S. K., Gertler, A., Broch, A., & Robbins, C. (2009). CRC Project No. AVFL-17 Investigation of Biodistillates as Potential Blendstocks for Transportation Fuels. Alpharetta: Coordinating Research Council
6. Eco Resources Consultants. (2012). Study of Hydrogenation Derived Renewable Diesel as a Renewable Fuel Option in North America. Ottawa: Natural Resources Canada.
7. Schwartz, M., Blakeley, K., & O'Rourke, R. (2012). Department of Defense Energy Initiatives: Background and Issues for Congress. Washington D.C.: Congressional Research Service.
8. Hartikka, T., Kuronen, M., & Kiiski, U. (2012). Technical Performance of HVO (Hydrotreated Vegetable Oil) in Diesel Engines. SAE Technical Paper 2012-01-1585.
9. Rathore, V., Newalkar, B. L., & Badoni, R. (2016). Processing of vegetable oil for biofuel production through conventional and non-conventional routes. Energy for Sustainable Development, 24-49.
10. Office of the Secretary of the Navy. (n.d.). Great Green Fleet. Retrieved from http://greenfleet.dodlive.mil/energy/great-green-fleet/ (accessed February 1, 2017).
11. John C. Stennis Strike Group Public Affairs. (2016, June 27). The Great Green Fleet Explained. Retrieved from http://www.navy.mil/submit/display.asp?story_id=95398 (accessed February 1, 2017).
12. Yost, D. (2014). Evaluation of Hydroprocessed Renewable Diesel (HRD) Fuel in a Caterpillar Engine Using the 210 Hour TWV Cycle. Warren: U.S. Army TARDEC.
13. Conkle, H., Marcum, G., Griesenbrock, E., Edwards, E., Chauhan, S., Morris, R., . . . Thomas, D. (2012). Development of Surrogates of Alternative Liquid Fuels Generated from Biomass. Dayton: Wright Brothers Institute.
14. Edwards, J. T., Shafer, L. M., & Klein, J. K. (2012). U.S. Air Force Hydroprocessed Renewable Jet (HRJ) Fuel Research. Wright-Patterson Air Force Base: Air Force Research Laboratory.
15. Conkle, H., Griesenbrock, E., Robota, H., Morris, R., & Coppola, E. (2013). Production of Unblended, "Drop-in," Renewable Jet Fuel. Wright-Patterson Air Force Base: U.S. Air Force.
16. Vassilev, S. V., & Vassileva, C. G. (2016). Composition, properties and challenges of algae biomass for biofuel application: An overview. Fuel, 1-33.
17. Santillan-Jimenez, E., Pace, R., Marques, S., Morgan, T., McKelphin, C., Mobley, J., & Crocker, M. (2016). Extraction, characterization, purification and catalytic upgrading of algae lipids to fuel-like hydrocarbons. Fuel, 668-678.
18. Pegallapti, A. K., & Frank, E. D. (2016). Energy use and greenhouse gas emissions from an algae fractionation process for producing renewable diesel. Algal Research, 235-240.
19. Ryskamp, R. (2016). Investigation of High Reactivity Fuel Property Effects on Reactivity Controlled Compression Ignition Combustion. 2016: West Virginia University.

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