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# Carbon profile matching, Algae fatty acids and Jet A fuel properties

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**Matching fuel carbon profiles to micro algae strain fatty acid profiles allows for a minimal refining, maximum productivity output. A calculator for estimating the properties of fuels from the algae components was created and applied to the production of 1 barrel equivalent per day of oil. The profile matching occurs by minimizing the sum of squared error (SSE) at each carbon number. A suboptimal solution with production fractions of 10% each for species CS256, CRF101, NT15, and 70% coconut was generated. The estimated properties are: a higher heating value of 38.6 MJ/kg, density of 0.87 kg/L, an approximately balanced unsaturated to saturated FAME ratio, and a 1.91 H/C ratio. For an estimated production level of 1 barrel of oil per day the land requirements are 51 ha of algae plate reactors. The proposed facility fixes 566 Mg of CO2 per annum. The fuel properties result in an estimated decrease of range for a hypothetical jet aircraft of 1.5%.**

## Nomenclature and Abbreviations

FAME = Fatty Acid Methyl Ester
FA = Fatty Acid
$F$ = Fuel Consumption
$R$ = Range, km
$CN$ = Cetene number, nondimensional
$HV$ = Heating Value of Fuel, $MJ/kg$
$H/C$= Hydrogen/Carbon molar ratio of fuel
$g$ = Acceleration due to gravity, $m/s^2$
$\eta_{tot}$ = Turbine efficiency
$C_L$ = Lift coefficient, nondimensional
$C_D$ = Drag coefficient, nondimensional
$W_1$ = Initial Mass, $kg$
$W_2$ = Final Mass, $kg$
$S$ = Wingspan area, $m^2$
$\rho$ = Air Density, $kg/m^3$
$c_T$ = Thrust Specific Fuel Consumption
*Subscripts*
$i$ = Algae subscript
$c$ = Molecule subscript
$b$ = Biofuel subscript
$s$ = Standard Jet A fuel subscript
*All measurements are reported on a dry weight basis unless otherwise noted.*

## I. Introduction

It is unknown exactly when oil production will enter an irreversible decline and literature is inexact[1 2] on the date. Aircraft are dependent on energy dense petroleum fuels for powered flight, and have been for the past 100 years. A lack of alternative liquid fuels leads to the possibility that powered flight will cease, both commercial and military. Meaning that the current fleet of aircraft may be the last. Carrier viability is strongly related to the price of jet fuel, the largest carrier expense. When prices rise, carriers are more likely to enter bankruptcy, become nationalized, or require restructuring. A means of decoupling carrier performance from the price of oil is highly desirable. Military applications also see strategic benefits[3]. Any means whereby one industry is able to decouple from the price of oil should be extensible to other industries, subject to the limits of suitable land, water, and nutrients. Microalgae are the historical source of oil[4 5] deposits today. They grow in brackish saline waters, on non-agricultural lands, and have high growth rates[6]. Large scale algae cultivation is one way to fill the imminent oil production gap without adverse effects on food crops.

Identification of all potential oil sources therefore essential to the future of manned air flight. There have been few algae flights to-date, including blends, making it of utmost importance to understand the fuel properties required for flight and how microalgae fatty acid methyl esters (FAME) can contribute. Each microalgae produces a distribution of different length fatty acid chains which are incorporated into triglycerides. The triglycerides are converted by transesterfication. The resulting fuel is relatively stable, and can be burned in various engines or turbines. By studying the final FAME fuel, property estimations and comparisons with standard (Jet A) aircraft fuels are possible. If the difference in molar concentration for each compound are minimized between a standard and surrogate, then the resulting surrogate fuel should have similar properties to the standard. Lacking a precise molar composition of FAME and Jet A the next best option is to compare the carbon atom profiles. A lack of precise quantification is due to outcome based testing, where final parameters of the fuel are examined (energy density, cetene value, boiling point, freezing point, flash point, etc), but the contribution of individual components is difficult to examine. Individual components are difficult to examine because of the combinatorial nature of all possible reactions. Jet fuel has hundreds or thousands of components, largely similar, but different enough that the effect of single components on larger scale properties was never attempted. Furthermore, the standard for jet fuel was created before the introduction of highly accurate high performance liquid chromatography linked mass spectrometers, meaning that careful composition analysis was 'skipped' because the fuel is taken for granted.

The refining of oil accounts for a significant amount of energy usage and the carbon profile matching, if it is able to predict suitable substitutes reduces and refining after the oil has been produced by algae. Oil production in the future is likely to revolve around heavier oil sands or heavy oils because the light-sweet crude sources have largely been exploited. The cost of refining thicker crude fractions is greater than the lighter fractions, making this matching strategy more viable. Reducing the costs of post-process refining is highly desirable. It represents the opportunity to produce algae oil, perform transesterfication, and directly utilize it on a plane. The pollution and cost associated with large refineries disappears.

### A. Considerations for flight

Consider a jet aircraft flying under steady state conditions at constant altitude. The steady state range equation[7] applies in this case. $R$ is the specific range of the aircraft, $W_1$ and $W_2$ are the initial and final weights of the aircraft, $C_L$ is the coefficient of lift, $C_D$ is the coefficient of drag, $c_T$ is the specific fuel consumption, $S$ is the wingspan area, and $\rho$ is the density of air.

$$R = \frac{2}{c_T}\sqrt{\frac{2C_L}{S\rho C_D^2}}\left(\sqrt{W_1} - \sqrt{W_2}\right) \tag{1}$$

As the plane burns fuel to maintain equal velocity the forces of drag and thrust are balanced. Thrust is provided by burning hydrocarbon fuels to turn the jet turbines of the aircraft and accelerate air. This imparts a velocity to the plane and the lift coefficient converts a fraction of this into a normal component. This normal component is the force keeping the plane in the air, the uplift force. The weight of the plane is accelerated by gravity towards the earth. It can be seen now that because the weight of the plane is decreasing, the lift force required is constantly decreasing throughout the flight time. The pilot, maintaining equal velocity and altitude is able to adjust the angle of attack of the wings so that less lift is produced. The result is that a lower weight aircraft does not have to burn as much fuel as a heavier one to stay at the same altitude and velocity.

At steady state, the hypothetical aircraft burns fuel to turn the jet turbines and balance the thrust and drag forces. For a given range the energy required for this trip is dominated by the parameters in equation 1. Now suppose this plane was refueled with a biofuel mix. Typical biofuels have energy densities equal or less than 40 MJ/kg[8] which decreases the flight range and impacts cargo and passenger carry capacity. To maintain an equivalent range with a lower heating value, a greater mass of fuel is required (assuming equal energy for the transit), demonstrating that the range parameter is strongly dependent on the heating value of the substitute fuel and the new weight of the aircraft.

### B. Jet A Standard

There are numerous fuel standards for aircraft. The properties and composition have been settled for 60 years. This report focuses on Jet A also known as JP-8. Similar standards are in use throughout Europe, Russia, and Asia. It should be noted that combat military aircraft run on different mixtures for performance reasons. Commercially purchased jet fuel does not adhere perfectly to the specified standards and with every load of fuel a certain amount of variance for each parameter is expected, with an increasing cost of fuel for a tighter specification adherence. Table 1 contains selected fuel properties of Jet A.

The fuel properties of primary importance are the freezing point, density, and net heating value[10]. If the fuel has a freezing point above ambient temperature (~-50°C for the typical passenger jet aircraft cruising altitude) fuel will solidify, starving the engines. At low temperatures, before the freezing point a similar effect can occur if fuel viscosity becomes too high. The H/C ratio is the hydrogen carbon ratio of the fuel. It is calculated by summing the atoms of carbon and hydrogen in the fuel mixture. Typical fuel tests combust a fuel with known quantities of oxygen, and the resulting compounds: CO2, H20, and various NOX and SOX are quantified using mass spectrometry. Using the these values and chemical equations hydrogen and carbon atoms present in the original fuel are calculated at a high degree of accuracy.

### C. Microalgae

Microalgae or microphytes are a group of diverse photosynthetic organisms. More than 30,000 have been discovered, and a few thousand have been studied. They are characterized by a lack of higher structure, existing as single organisms, pairs (diatoms), or short linked chains. Lacking higher order structures such as roots, leaves, and branches the smaller organisms are dependent on their immediate environment for growth. They are not capable of surviving outside of the environment they have evolved to survive in. This means that controlling the conditions for growth is critical to maximize biomass growth. Important parameter for maximum growth[11] include: hydrodynamic limits, light levels, pH, dissolved $CO_2$, dissolved $O_2$, salt content, temperature, micro, and macro nutrients. The most important factors are: light, $CO_2$, $O_2$, and hydrodynamic limits.

**Table 1. Typical Jet A properties, taken from Edwards[9] .**

| Property | Magnitude |
|---|---|
| Formula (approximate) | $C_{11}H_{21}$ |
| H/C ratio | 1.91 |
| Boiling Point (°C) | 165 - 265 |
| Freezing Point (°C) | -50 |
| Net Heating Value (MJ/kg) | 43.147 |
| Density (kg/L) | 0.81 |

Increasing light levels increases growth up to the saturation point where the algae photocentres cannot use any more energy. Illumination at levels above the saturation point decrease growth and damage the photocentres. After damage the cell requires a period of darkness to recover[12]. This recovery period is controllable using agitation or mechanical shutters to generate artificial dark/light cycles. Agitation is the ideal method, as it improves mass transfer without limiting total incident solar radiation to the culture. Microalgae shear stress tolerances dictate the maximum agitation levels, too high and the cells break apart reducing growth again. Combined over saturation of light and high $O_2$ levels causes photo-oxidation of cell compounds and inhibits the carbon fixation cycle. High $O_2$ levels are likely to coincide with low $CO_2$ levels, proper degassing methods are critical to high production systems.

One common method to improve oil yields from algae is through the manipulation of the macronutrient nitrogen. The technique is called nitrogen starvation, where insufficient nitrogen for maximum biomass growth is provided to the culture. The stress causes algae composition to shift towards triglycerides while decreasing biomass growth. Careful nitrogen control and algae oil production monitoring are required to ensures that the rate of overall oil production rate has actually increased.

Ideal microalgae for aviation fuel production have high biomass growth, a large lipid proportion, are tolerant of high salt levels, and are able to photosynthasize efficiently under a wide variety of light conditions. These goals are difficult to reach because of organism limitations and cost constraints.

### D. Cultivation systems.

The largest capital cost in an algae installation is the use. The cultivation of microalgae occurs either in open or closed photobioreactors. The most common system is the raceway pond, an open reactor. The depth of the reactor is between 20 and 30 cm, depending on light penetration and algae. A single paddle wheel ensures agitation of the algae. This style of system is popular among researchers and some commercial startups because they are cheap to construct and maintain. The current largest open pond reactor grows algae for feeding juvanile farmed fish. These systems suffer from lower than expected biomass growth rates. Competition from environmental organisms, poor $CO_2$ capture, and low cell density contribute to low growth. Open systems are more unpredictable than closed ones, and a considerable amount of water evaporates and requires replacement each day.

More capital intensive closed systems are called photobioreactors. The photobioreactor are classified as tubular, plate, or annular[13]. Tubular systems consist of transparent tubes (glass or plastic) oriented vertically, horizontally, or helically with algae pumped through. The two largest differences between various reactors are the required fill volumes and mass transfer characteristics. Annular systems are similar to tubular, only containing another smaller concentric tube. This reduces the volume of growth medium and allows for atypical or unique lighting situations. Typical lighting consists of constructing the photobioreactor outdoors and allowing natural sunlight to drive growth. In this scenario light at the surface of the reactor is greater than at greater depth. An example of a unique lighting situation is a vertically oriented annular tube that used mirrors to direct light down the annular space. The culture received lighting from two sides. This specific method is referred to as an internal illumination scheme. This was judged impractical for larger installations due to higher costs and complexity. Plate reactors are simple systems, thin reaction vessels that cover significant area. They are also orientable like solar panels, increasing radiation capture. These plates are enclosed, and orientable to capture a maximum amount of light. The disadvantage is the cost of cooling such a system. To date record biomass production is on the order of 50 $g/(m^2 day)$ biomass from a flat plate reactor[14].

Before extraction the algae mass is filtered and dried. The medium is returned to the culturing system and the algae mass is dried passively or actively. Passive drying is conducted by placing the algae in the sun for a couple days. Mold and the long drying times render this method infeasible except for very hot and dry locations. Active drying involves a dehydration furnace at greater expense and fossil fuel usage. The dry algae are pulverized and washed with a polar solvent, typically hexane. The solvent extracts the oils and is recovered later. The triglycerides must be free of water for optimal transesterfication. After the algae are dried and the oil extracted, the remaining biomass is highly desired for animal feed, recycled into the nutrient medium, or pyrolysized to generate useful downstream products. The spent algae can also be burned to fuel the drying furnace, but have higher value as cattle feed.

### E. Transesterfication

Typical reaction conditions are a 3:1 molar ratio of ethanol to fatty acids, a base, and catalyst (Figure 1). Even conducted at low temperatures over several hours the reaction has high molar yields (99.7%) with the products as FAME and glycerol. The high molar yield means that the reaction consumes 99.7% of the triglycerides to produce end products in their respective molar ratios. Any low molecular weight alcohols are suitable for this reaction but the reaction of higher molecular weight alcohols with triglycerides is less efficient, meaning that there will be triglyceride left at the end of the reaction. The higher the weight of the alcohol, the greater the decrease in reaction efficiency. The produced glycerol is progressively removed by repeated washing with clean water because it is soluble and the FAME are not.

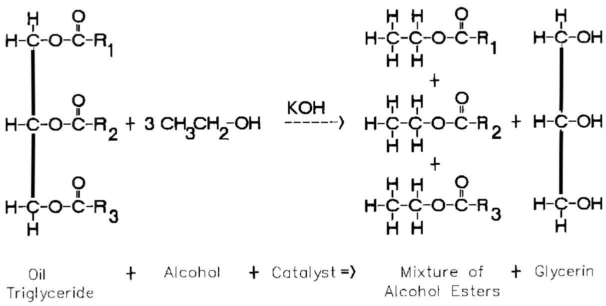

**Figure 1. Transesterfication reaction with methanol, the products are FAME and glycerol. Extra carbons not shown, taken from[15].**

Plant oils are transesterfied in an identical reaction and have been used for biodiesels production. Prominent examples include soybean diesel, coconut oil, and palm oil. The latter two are from tropical climates, where the soybean is growth throughout Europe and across the center of North America.

## II. Method

Microalgae fatty acid profiles of 20 algae were obtained[16][17]. A dozen common plant oil profiles were also obtained for comparision. Production rates were changed to an areal productivity (g oil / $m^2$ day) measurement from whatever basis was expressed assuming a 2.5cm annular spacing for the plate photobioreactors. Employing a conservative approach, no increased productivity was applied with respect to altering the plate annular space, as has been previously demonstrated[14].

The hypothesis is that if the carbon atom profile of a standard fuel is matched to a surrogate lipid fuel that the properties of the surrogate are estimable from the quantities of each constituent. The carbon atom profiles of various jet fuels: Jet-A, RP-1, JP-7, and diesel are given by Edwards[9] , only Jet-A data was replicated in table 1.

### A. Fuel Property Model

Using the fatty acid profiles, the collected properties of the final transesterfied fuel properties were estimated. The fatty acids were considered as FAME. The properties of FAME were taken from literature when available[18][8][19], and estimated otherwise[20]. A linear weighted average of the carbon atom profile was constructed from the fatty acid profiles. $Oil$ refers to the percent distribution of molecules of size $c$ carbon atoms for the $i$'th algae, $X$ represents the composition of a specific algae, and $n_i$ is the fraction of production area devoted to the $i$'th algae.

$$Oil_{i,c} = \sum_{i=1} n_i \, X_{c,i} \tag{2}$$

The properties were estimated from the resulting oil composition from equation 2 using equation 4 below where $P$ is the property to estimate by summing the weighted properties of the different carbon length FAME molecules $c$. The estimated properties are heating value of fuel, density of fuel, and the hydrogen carbon ratio $P \epsilon \{HV,\ \rho,\ H/C\}$.

$$P_{est} = \sum_{i=1} Oil_{i,c} \, P_c \tag{3}$$

All fatty acid distributions retrieved did not sum to 100%, therefore an oil productivity correction factor was established, whereby only identified oil fractions contribute towards growth. The correction factor ($CF$) penalizes oil productivity for poorly-characterized algae in a linear fashion.

$$CF_i = \sum_{c=1}^{n} X_{c,i} \tag{4}$$

$CO_2$ fixation, water consumption, and fertilizer requirements are calculated from the approximate biomass formula $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$[21]. All algae were considered to have identical formula, no specific formula were available for the algae considered. Plant oil profiles[22 23] were included to fill in any oil profile gaps. Areal oil production[21] was used, and no plant biomass growth was considered.

### B. Aircraft Range

The range of an aircraft using a different fuel is found by modifying equation 1. As the planes being considered are equal, and only the range changes, equate the conditions using $\Omega = \frac{2}{c_T}\sqrt{\frac{2C_L}{S\rho C_D^2}}$ as the actual aeroframe which governs the drag, lift, and wingspan is the same. As the alternative fueled flight is flying at the same altitude, the density of the air is the same. Therefore generate two equations for $R_s$ and $R_b$. The subscript $s$ means standard flight, and $b$ means a biofuelled one.

$$R = \Omega\left(\sqrt{W_1} - \sqrt{W_2}\right) \tag{5}$$

$$\frac{\left(\sqrt{W_{b,1}} - \sqrt{W_{b,2}}\right)}{\left(\sqrt{W_{s,1}} - \sqrt{W_{s,2}}\right)} = \frac{R_b}{R_s} \tag{6}$$

The difference in range, assuming equal energy consumption per km flight is now calculable. To maintain equal thrust, fuel consumption must change (increase for lower energy fuels proportional to the difference in energy content!). Therefore adjust the range $R_b$ by $\frac{HV_b}{HV_s}$, here $HV_b$ is the higher heating value of a biofuel, and $HV_s$ is the higher heating value of the standard Jet A fuel. The final equation is given below.

$$\frac{\left(\sqrt{W_{b,1}} - \sqrt{W_{b,2}}\right)}{\left(\sqrt{W_{s,1}} - \sqrt{W_{s,2}}\right)}\left(\frac{HV_b}{HV_s}\right)R_s = R_b \tag{7}$$

Range alterations were calculated on the 747:300 airframe produced by Boeing. This aircraft was chosen because of its widespread recognition and long flight history. Parameters were obtained from Boeing and are listed in Table 2. Final weights are taken as the maximum safe takeoff mass less the mass of fuel burned. The range calculation was done for equivalent fuel capacities, meaning that fuel volumes above 199 158 L are forgone.

**Table 2. 747:300 Airframe Parameters**

| Parameter | Magnitude |
|---|---|
| Empty Mass (kg) | 178 100 |
| Maximum Save Takeoff Mass (kg) | 377 842 |
| Jet A Fuel Capacity (L) | 199 158 |
| Range (km) | 12 500 |
| Flight Energy (MJ) | 6 900 000 |

## III. Discussion

Two primary models were examined, one where the difference between a surrogate and the standard was minimized to see *how close* the fuel properties are. The second was performed to maximize oil production overall, to demonstrate how algae profiles are not particularly well suited as oil replacements.

The closest fuel surrogate is presented in figure 2, it is comprised of 10% CS256, 10% CRF101, 10% NT15, and 70% coconut oil. This blend includes a plant fraction to increase the similarity of the surrogate to Jet A. The approximate production was 3.48 $g\ m^{-2}day^{-1}$ biomass. The required land for algae production is approximately 51 ha of land. Total oil was 10.1% of biomass by weight. Adding a large fraction of coconut oil, which contains lower carbon molecules, significantly decreased the sum of squared error. The energy density was 38.6MJ/kg and a density of 0.867 kg/L was achieved. There were approximately equal saturated and unsaturated FAME. A calculated range reduction was 1.5%. The hydrogen carbon ratio was calculated at 1.91 H/C.

Maximizing the oil production rate of the model through 100% allocation of the CS256 strain results in 18 ha of area producing 7.58 $g\ m^{-2}day^{-1}$ of biomass. This is roughly equal to large raceway pond systems. The oil fraction is described in figure **??**, total oil comprises approximately 13% of the biomass by weight. The proposed fuel surrogate is estimated to have an energy density of 40.4 MJ/kg, a density of 0.891 kg/L, and a majority of unsaturated FAME. Unsaturated FAME reduce the viability of this fuel as it will be prone to oxidation and poor long term stability. The range decrease as calculated from equation 7 is 2.0%. The hydrogen/carbon ratio was calculated to be 1.83 H/C.

From an examination of the algae fatty acid profiles they are dominated by chain lengths greater than 14 carbon atoms. Of the species studied, none had fatty acids of length less than 14. From the Jet A profile a low proportion of molecular species have carbon counts greater than or equal to 14. It is unknown if this is an analysis limitation, because as mentioned some of the fatty acid totals do not sum to 100%, or if algae evolved longer chain FA out of necessity. The large error in profile matching exists due to lack of combined algae fatty acid profiles and growth characterization. The conclusion from the fatty acid profile characteristics indicates that significant decreases in refining requirements are not possible with the 20 species studied. Only through the introduction of tropical plant oils (coconut) could the surrogate gain a similar carbon atom profile.

Theoretical photosynthetic microalgae maximum growth rates are estimated at 68.5 $g\ m^{-2} day^{-1}$ on a dry weight basis[24]. Literature growth rates reported[16] and outputs of this model are significantly below this level indicating that substantial improvements are possible through growth optimizations not utilized in the model. Improvements would decrease the areal land requirements for growth and decrease overall costs. Obtaining sufficient carbon dioxide is likely to be a limiting factor as the productivity of microalgae cultivation increases. CO2 enrichment[25] from power plants flue gas is possible assuming it is scrubbed of toxic compounds. Algae farms would become more cost competitive with carbon credits or taxation, whereby for each ton of carbon the algae cultivator receives 20 to 40 USD depending on the market rate or subsidy amount. This would offset 10% of the biomass costs[26].

The commercial potential of 18:1, 18:2, and 18:3 - the omega fatty acids - means it is more profitable to sell this fraction as a supplement than as fuel. Density and net heating value give the volumetric heating value, if this is lower than normal, the fuel takes up more space, necessitating less cargo or passenger room. Two practical and significant production increases are obtained through increased radiation capture by incident angle changes and a reduced annular space of the plate reactor. Detailed studies by Qiang[27] and Hu[14] a combination of decreased annular space and 4 tiltings per year doubled biomass production during the testing period. This represents a significant boost, taking the maximum production in this paper up to 15 grams biomass per meter squared day. Chisti[21] indicates that biomass production of some 30-50 grams per day meter squared at 50% oil composition, year-round are required for commercial competition with petroleum in the United States. Production levels here are competitive with prices in nations with heavy petroleum taxes (most of Europe especially Norway) but no assessment of the overall production costs was made.

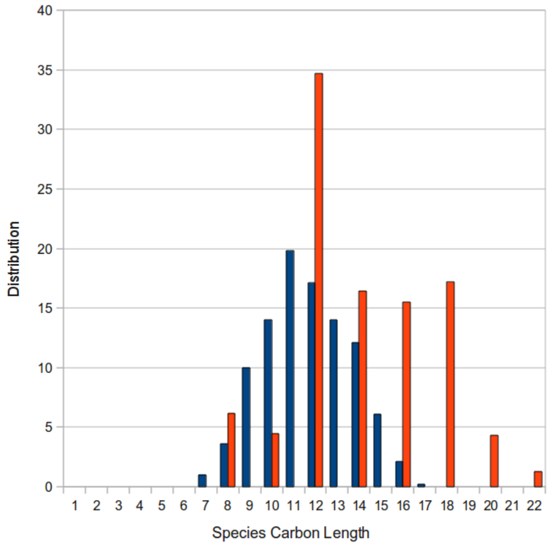

**Figure 2. Carbon Atom Profile: Minimized carbon profile error of a mixture of algae. Red is the surrogate, blue is carbon atom profile of Jet A. Estimated properties 38.6 MJ/kg, 0.869 kg/L, 1.91 H:C, and 51% unsaturated, 49% saturated FAME.**

Direct use of 100% algae biofuels in aviation is unlikely at this time even with airplane modifications. The obvious modifications, increased fuel tank volume or active temperature control are unlikely to solve this problem for the following reasons: (1) Modification of the aeroframe to accommodate insulation or increases in fuel volume necessitate structural changes which adversely impact drag. (2) Internal modification of cargo/passenger space reduces the carrying capacity of the plane and economic competitiveness. (3) Active temperature control requires burning a quantity of fuel, the heat of which is likely to conduct away to the skin of the aircraft where it is drawn away by the wind. Fuel is also required for temperature maintenance. The optimal solution is to generate a replacement fuel which has a similar properties compared with Jet A.

The model is incomplete, and this only represents the first steps towards a decision making tool for siting and allocating algae strains for growth. A more critical examination of the effects of changing fuel constituents on the final fuel properties is desirable. Increased numbers of algae strains and a standardized method of determining growth rates is required. No standard method and apparatus has been settled upon, and as a result the data is needlessly difficult to manipulate and compare. A lack of lower molecular weight fatty acids causes significant problems with profile matching. If no algae exist with lower chain length fatty acids, genetic engineering can play a significant role in creating ideal microalgae. It may be advantageous to extend the presented model and augment it with various predictive models for: viscosity[22], combustion[28], cetene and many more proposed by Knothe[8].

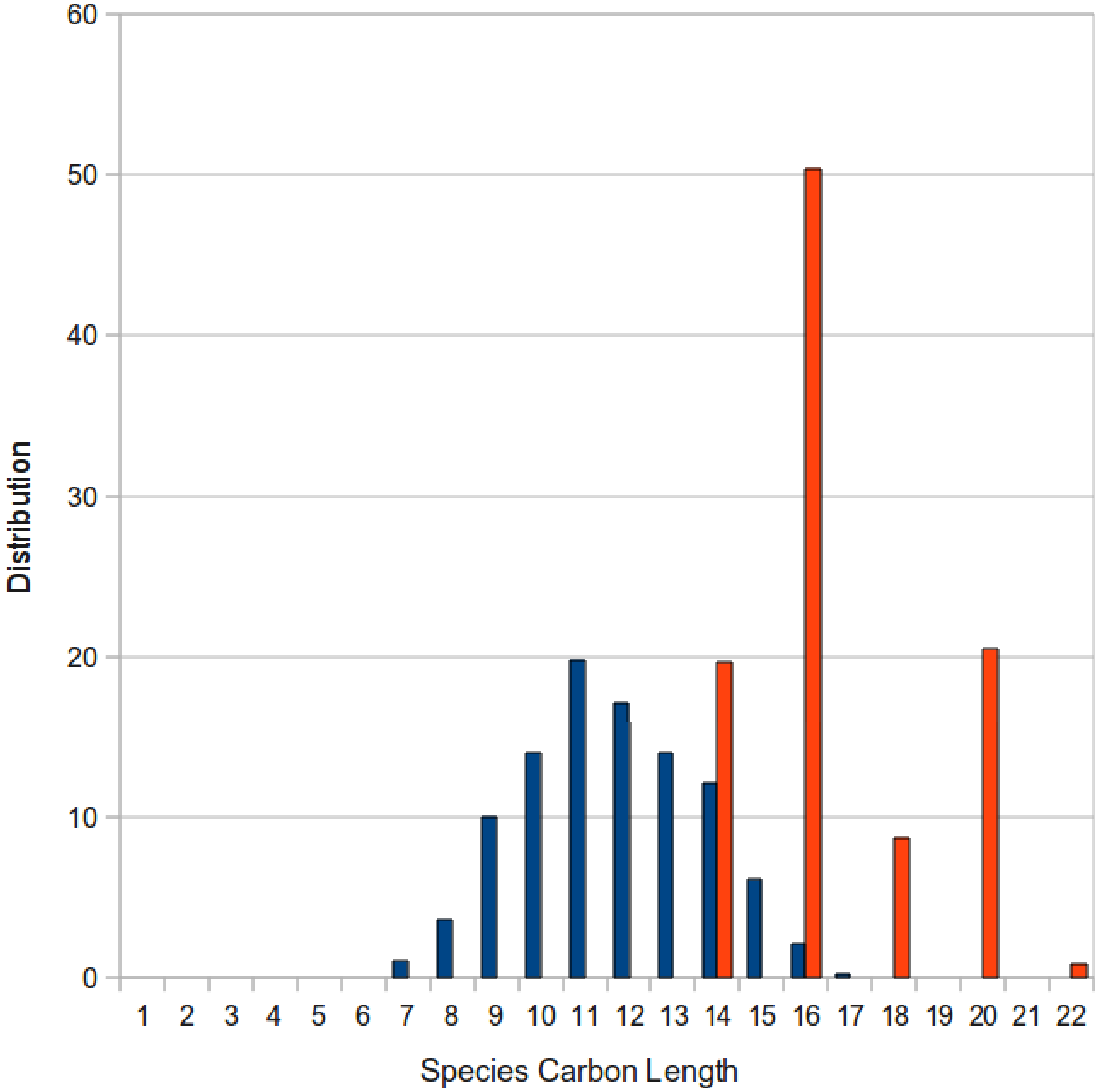

**Figure 3. Carbon atom profile: Maximum oil production by a single strain of algae. Red is the surrogate, blue is carbon atom profile of Jet A. Estimated properties 40.4 MJ/kg, 0.891 kg/L, 1.83 H:C, and 75% unsaturated, 25% saturated FAME.**

# IV. Conclusion

A novel method for selecting algae strains to replace a fossil fuel is outlined and demonstrated. The model was applied to Jet A production and resulted in inferior heating values, greater density, and lower H/C ratios. The fuel was mostly unsaturated FAME, which will result in poor long term fuel stability. There are a number of obvious deficiencies which are addressable through further research. As more algae profile and growth information becomes available, the utility should improve over time as it is extended to more reactors and predict a greater number of fuel properties.

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