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# Energy and carbon accounting to compare bioenergy crops

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To compare the utility of current and future biofuels and biofuel feedstocks in an objective manner can be extremely challenging. This challenge exists because agricultural data are inherently variable, experimental techniques are crop-dependent, and the literatures usually report relative, rather than absolute, values. Here, we discuss the 'PETRO approach', a systematic approach to evaluate new crops. This approach accounts for not only the capture of solar energy but also the capture of atmospheric carbon (as CO<sub>2</sub>) to generate a final carbon-based liquid fuel product. The energy yield, per unit area, of biofuel crops grown in different climate zones can thus be benchmarked and quantitatively compared in terms of both carbon gain and solar energy conversion efficiency.

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## Introduction

In production of liquid fuels, the enormous barriers that face plausible substitutes for fossil fuel sources are derived from two factors: the lowest-cost economics of commodities and the logistics of implementation of new technologies at immense scale. These barriers make the development of alternatives to petroleum one of the most challenging problems faced by human society [1]. Several credible approaches seek to exploit other non-renewable resources, such as the use of natural gas in vehicles or the conversion of coal-derived or gas-derived syngas to drop-in synthetic fuels via the Fischer–Tropsch process. Other approaches seek to shift from internal combustion engines to electric motors, a shift that increases the number of substitutes for petroleum-based energy. However, even electric vehicles such as the Chevrolet Volt or the Nissan Leaf

are not substantially more environmentally friendly or sustainable compared to conventional vehicles when connected to an electrical grid dominated by non-renewable carbon-emitting generation facilities [2].

In theory, strategies that produce renewable biofuels both at low cost (relative to increasingly scarce petroleum) and at large scale will help lead to a cleaner, more sustainable future. However, transitioning to a higher share of renewable biofuels carries profound implications: On a fundamental level, photosynthetic biofuels replace the process of mining (i.e. underground energy extraction) with the process of agriculture (i.e. above-ground energy capture). Such a process shift is significant, not only because the methods of energy harvesting are divergent, but also because biomass has both significantly lower energy density and significantly higher carbon oxidation state than crude fossil energy feedstocks.

The energy stored in biofuels is derived from current biological carbon fixation, a process that accounts for nearly all of the gross primary production of the planet and at least half of the annual global absorption of atmospheric carbon dioxide [4]. Biofuels can be formed from terrestrial plant matter, by the aquaculture of cyanobacteria, microalgae, or macroalgae, or even by the non-photosynthetic fixation of carbon by chemolithoautotrophs [5]. All of these approaches essentially reverse the combustion of carbon-based liquid fuels, using an external energy source to convert carbon dioxide into energy dense hydrocarbons. This process is complex but is fairly well understood in terms of energy capture, carbon yield, and process economics. For the past 2.4 billion years (nearly half the age of the earth) [6], photosynthetic biology has acted to reduce atmospheric carbon concentrations and increase atmospheric oxygen using energy from sunlight and electrons from water to sequester carbon into more highly reduced compounds, providing the basis for life on the planet<sup>4</sup> as well as storing energy in previous geological era as fossil fuels.

Conventional genetic selection has significantly improved the yields of biomass crops [7], while the technologies for engineering crops with improved agronomic properties have begun to mature more rapidly [8].

<sup>4</sup> We explicitly note that several other critical inputs, such as nitrogen, phosphorus, sulfur, and water (used other than as a source of reducing equivalents) should be considered when performing a full life cycle analysis of any biological system intended for biofuels production. In this article, however, carbon and light energy will be considered the sole primary inputs.

Tools to engineer biological systems for higher productivity have been developed in microbial systems [9], providing a tantalizing prospect to engineer energy crops with characteristics more favorable for energy capture.

The development of methods to engineer energy crops is necessary, but not sufficient, to impact the future of renewable biofuels. Technologies to measure and model the impact of proposed engineering improvements in complex biological systems are also needed. These methods are nearly impossible to validate, because they depend heavily on assumptions of energy flows and rates of individual steps within particular parts of the organism, built from *ex vivo* or laboratory measurements. Biochemical optimization of photosynthesis builds up from the biological or biochemical components of the system [e.g. [10]], while agronomic optimization of biomass yields is derived primarily from domestication and breeding of wild plant varieties. These paths must eventually converge.

As a positive step in this direction, while developing the Plants Engineered To Replace Oil (PETRO) program, ARPA-E developed a holistic approach that looks simultaneously at both energy and mass balances to evaluate different paths toward improved, dedicated, renewable biofuels crops. This 'PETRO approach' provides a means for tracking both energy and carbon from solar photons to liquid fuels.

## Fundamentals

The modern diversity of photosynthetic organisms derives from the capture of a cyanobacterium by a eukaryotic cell as a protochloroplast [11]. Essentially, the fundamental biochemical structures and pathways used to capture and store solar energy (i.e. the RuBisCO-based carbon reduction cycle) was inherited by eukaryotes from endosymbiotic cyanobacteria resulting in the adoption, by plants, of a biochemical strategy for carbon assimilation that has been conserved over the past 2 billion years [12]. As a consequence, carbon capture and storage varies only slightly from one plant species to another, primarily in the differentiation among C<sub>3</sub>, C<sub>4</sub>, and CAM plants [13]. However, subsequent to the highly conserved process of photosynthesis is an immense metabolic diversity shaped by species, environment and development, which has created profound differences in the bioproducts of different plants under different environments at different developmental stages. While the carbohydrates in biomass have been a primary target for conversion into fuels due to their abundance in the biosphere, the relatively high oxidation state of carbon in these molecules (nominally 0) [3] mandates either the addition of reducing equivalents or the loss of carbon in a higher oxidation state, if an energy dense fuel is to result. This contrasts

with processing of traditional fossil-derived hydrocarbons (the carbon oxidation state of methane is  $-4$ , alkanes are  $-2$  to  $-3$ , while gasoline is about  $-1.7^5$ ). Energetically (and therefore economically) costly conversion steps are thus unavoidable when starting with biomass, if the target is a more energy dense (less oxidized) fuel. Fortunately, many plants already produce natural products with lower oxidation states and thus higher energy value (e.g. lipids, terpenes) [14], but their amounts can vary widely both among plant species as well as within the different tissues of a given plant, complicating the calculation of energy yields.

## Where we are today

An accurate, quantitative analysis of biological systems, accounting for both process and economics, would allow comparative analysis of new biofuel crops, but a systematic methodology is currently lacking. Economic performance metrics in bioenergy (e.g. 'barrel of oil equivalent', 'tons of biomass per acre', 'feedstock costs') are frequently used, but these metrics tend to finesse the central issue of objective comparison. Different disciplines, and even different research groups within a particular discipline, make different assumptions and use different comparators in the calculation of efficiencies and yields. Key physical data, including feedstock composition (particularly moisture content), seasonal yields, regional climatic conditions and year-over-year variability, are frequently not reported. These reporting inconsistencies make it difficult to derive an objective basis of comparison from diverse literature sources. What is needed is a detailed accounting of the flow of both energy and mass from raw materials (sunlight, carbon dioxide, and water), through a conversion process (plants), into finished goods (fuel). This requirement implies a model based on chemical processes, with a series of connected steps that each has inputs, outputs, and conversions. This system is usually discussed in terms of energy flow, where energy losses are tracked from inputs to output, with conversions described in terms of efficiency [15]. However, there is another key dimension, beyond the transduction of light energy: the flow of carbon from atmospheric capture to conversion into bioproducts. Carbon dioxide is absorbed from the atmosphere and proceeds through a series of conversion steps to produce a liquid fuel. These processes happen both during the growth of the plant and during the processing of biomaterial after harvest. This stepwise formalism promotes a discussion on the basis of standard units (e.g. tonnes of carbon per hectare per year,  $\text{Mg}_C \text{ha}^{-1} \text{y}^{-1}$ ) and on the chemical stoichiometry of

<sup>5</sup> The oxidation state of carbon in gasoline is, necessarily, an approximate number due to the variability in crude oil composition from different wells and processing at different refineries. This number has been estimated here by taking the weighted average of the nominal oxidation states of typical gasoline mixture constituent molecule classes, assuming 60% alkanes (carbon oxidation state nominally =  $-2$ ), 30% aromatics (carbon oxidation state nominally =  $-1$ ), and 10% oxygenates (carbon oxidation state nominally =  $-1$ ).

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