# Bio-oil Sequestration

Prototype Protocol for Measurement, Reporting, & Verification

Overview

This proto-protocol is intended for use within voluntary carbon markets. Bio-oil sequestration involves the conversion of waste biomass to bio-oil via processes such as fast pyrolysis[1], followed by injection of the bio-oil into deep geological formations for permanent storage. "Bio-oil" is intended here to broadly encompass fast pyrolysis oil, biocrude, slurries containing biochar, and other organic compounds derived from biomass.

Over 100 Gt CO_2[2] is exchanged between the atmosphere and biosphere annually via photosynthesis, respiration, decomposition, and combustion. Through appropriate selection of biomass residue feedstocks that would otherwise decompose or combust, the conversion of biomass to bio-oil and the permanent geological storage of the embodied carbon is a net removal from the atmosphere.

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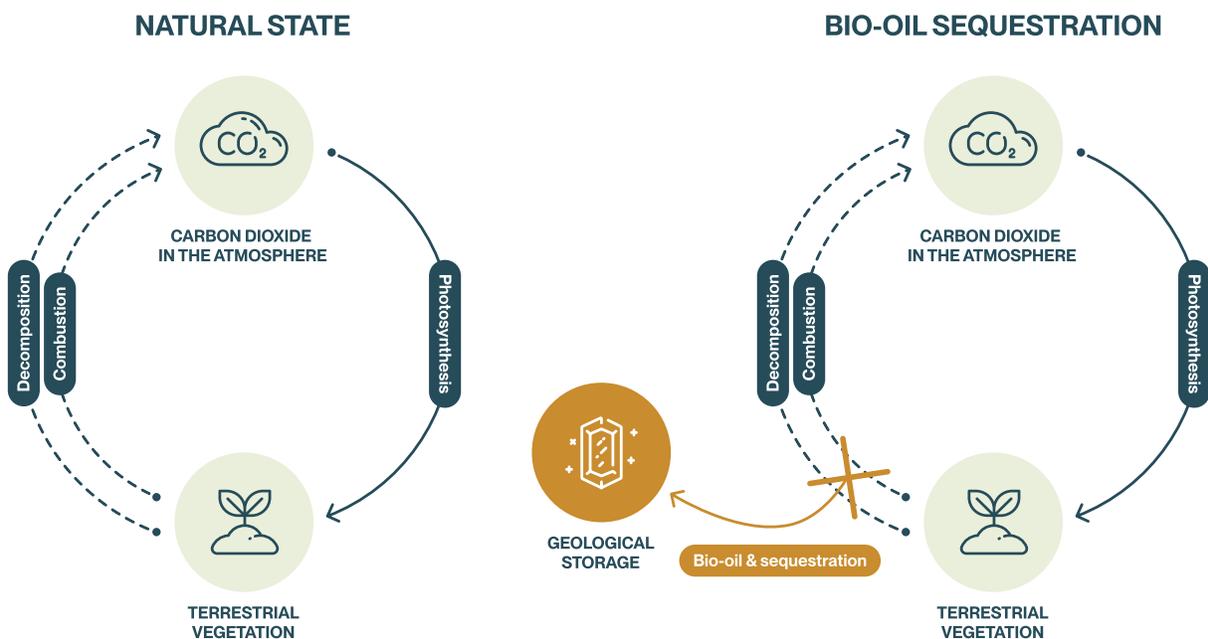
1   Fast Pyrolysis is a method of heating organic material to high temperatures in the presence of little or no oxygen to produce syngas, bio-oil, and biochar. Other processes, such as hydrothermal liquefaction, can also produce bio-oils.

2   Biomass: Impact on Carbon Cycle and Greenhouse Gas Emissions, Carly Green, Kenneth A. Byrne, in Encyclopedia of Energy, 2004

Measurement and verification are essential to credit any process claiming carbon sequestration; without them, any claims that carbon is being permanently removed from the atmosphere are suspect, and could result in unaccounted reversal and possible environmental and commercial penalties.

This proto-protocol outlines a framework for measuring, reporting, and verifying (MRV) bio-oil sequestration.

Process Flow and Carbon Accounting

SYSTEM BOUNDARIES

Measuring the amount of carbon captured and sequestered relies on life-cycle analysis (LCA); an LCA study involves establishing baselines and conducting a thorough inventory of the energy and materials required by all the processes involved in capturing and sequestering the carbon and calculating their corresponding greenhouse gas (GHG) emissions to the environment. An LCA assesses cumulative potential environmental impacts and is conducted only for processes within set system boundaries.

For instance, life cycle analysis for renewable diesel made from soy oil typically includes measuring emissions resulting from the following processes:

- Farm practices involved in growing and harvesting soybeans (biomass production)
- Soybean transportation to the crush plant (biomass transport)
- Soybean crushing and oil extraction (biomass conversion)
- Transportation of soy oil to a renewable diesel facility (biomass transport)
- Renewable diesel production (biomass conversion/fuel production)
- Transportation of the finished fuel to its destination (fuel transport)
- Combustion of the renewable diesel (fuel end use)
- Direct or indirect land-use changes resulting from growth of soybeans (biomass production)

If the project were to capture and sequester the CO_2 produced during the fuel production stage, the LCA would include measuring emissions from the following additional steps:

- CO_2 capture at renewable diesel production
- CO_2 liquefaction and transport to sequestration facility
- CO_2 injection into storage
- Monitoring costs and measured CO_2 returns

In the case of bio-oil sequestration, system boundaries include emissions resulting from the following processes:

- Biomass production and collection, including direct and indirect land use change
- Transportation of biomass to the facility
- Conversion of biomass to bio-oil
- Transportation of the bio-oil to the sequestration facility
- Subsequent injection into a geological formation for storage and potential leakage

In some cases, if the biomass were to be transported to an alternate disposal site in the baseline, the net difference for the transportation to the facility may be compared to the baseline and accounted for.

This protocol does not consider production of co-products, such as biochar and energy products such as heat and electricity. No deductions are given for displacement from co-products. Correspondingly, all increases in upstream biomass emissions from the baseline are allocated to the bio-oil product.

CALCULATION OF NET CARBON REMOVAL

Analyses of life cycle emissions, such as the one above, are estimated using models and inventories, some of which have been adopted by regulators such as the California Air Resources Board (CARB). CARB has a protocol for CO_2 sequestration[3] that is integrated with the Low Carbon Fuel Standard (LCFS) regulation[4]. CARB's LCA for fuels is conducted using measurements of emissions and calculations based on actual biomass transportation, production, transportation, conversion and fuel end use/disposal data.

Bio-oil production and sequestration require biomass and energy inputs and outputs of stored carbon (bio-oil), CO_2 (from conversion, transport, and injection energy use), biochar (by-product), and low volumes of other GHGs. Once an LCA model is created, then the net amount of removed CO_2e is calculated as:

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\begin{aligned}
\text{Net Removed } CO_2e = &\sum CO_2e \text{ in the injected bio-oil} \\
&- \sum CO_2e \text{ emissions from biomass production} \\
&- \sum CO_2e \text{ emissions from biomass collection} \\
&- \sum CO_2e \text{ emissions from biomass transport} \\
&- \sum CO_2e \text{ non-process-biomass emissions from the conversion process} \\
&- \sum CO_2e \text{ of non-}CO_2 \text{ biomass-based process emissions} \\
&- \sum CO_2e \text{ emissions from bio-oil transport} \\
&- \sum CO_2e \text{ emissions from bio-oil injection} \\
&- \sum CO_2e \text{ from fugitive emissions}
\end{aligned}
$$

The LCA baseline is grounded on baseline measurement and assessment in the absence of the project. In some cases, for example, waste biomass which serves as biomass feedstock for the project would be left in its natural environment, such as the field or forest floor, or transported to landfills, where it would decompose and produce CO_2 and methane. Instead of these greenhouse gasses being released into the atmosphere in the baseline scenario, bio-oil production and injection sequesters CO_2e underground.

In calculating the CO_2e emissions from biomass production, feedstock specific pathways are required. These pathways capture emissions impacts of biomass utilization for the project as compared to the baseline. For example, in-field corn stover degradation can contribute to the nutrient content in the soil and its removal may result in an additional fertilizer requirement during the planting season. Any actual increase in fertilizer use would contribute to the CO_2e from biomass production and must be included in LCA.

If the baseline for the biomass is landfilling or decaying under anaerobic conditions, there may be production of methane in the baseline, a greenhouse gas with a high global warming potential (GWP). The LCA for the process should track reduced methane if measured, but not include avoided methane as part of the CO_2e balance calculation (instead, that should be tracked separately due to uncertainty around methane generation counterfactuals and future accounting practice).

The timing of decomposition and subsequent GHG release associated with the baseline scenario is dependent on several factors. Studies on corn stover, for example, show 60-70% of the biomass decays within the first year, and 75-80% by year 2, and 80-90% by year 5[5]. Physically, the decomposition timing is short with respect to the long arc of climate change and project lifetime, and can be safely ignored from an impact perspective. Similarly for accounting purposes, consistent with established methodology such as the World Resources Institute's GHG Protocol's guidance related to dead organic material (DOM), the timing delay associated with the baseline case CO_2 emissions from degradation does not require amortization across the years in which the degradation would have otherwise occurred, and is appropriate to be claimed at the time of intervention[6].

Industry standard methodologies exist (such as the Argonne National Laboratory GREET models used for biofuel LCA) to calculate the material and energy flows for biomass production arising from factors such as decreased soil carbon intensity

3 https://ww2.arb.ca.gov/sites/default/files/2020-03/CCS_Protocol_Under_LCFS_8-13-18_ada.pdf

4 https://ww2.arb.ca.gov/sites/default/files/2020-07/2020_lcfs_fro_oal-approved_unofficial_06302020.pdf

5 https://cdnsciencepub.com/doi/10.4141/cjss2010-055#T0002

6 https://ghgprotocol.org/sites/default/files/standards/GHG%20Protocol%20Agricultural%20Guidance%20%28April%2026%29_0.pdf

or increased fertilizer replacement rates[7]. These flows will be used to calculate the emissions impact associated with biomass production and will be added to the total emissions for the LCA. Industry standard methodologies must be applied to calculate the biomass production emissions based on specific project attributes, including the location and biomass type.

LAND-USE CHANGE (DIRECT AND INDIRECT) CONSIDERATIONS

Direct land use change occurs when landscapes are altered for biomass production. For instance, a forest may be cleared to support production of a new biomass crop, or an annual cropping system may transition to a perennial cropping system. Indirect land use change occurs when other landscapes are altered as a consequence of biomass production through market-mediated effects. For instance, a forest may be cleared as a result of higher prices when food-producing land is diverted to produce biomass or carbon removal services. Estimates of indirect land use change for common crops have been estimates by the CA ARB[8], while estimates of both direct and indirect land use change have been included in the GREET model[9]. Direct and indirect land use change must be estimated as part of each feedstock-specific pathway.

SUMMARY

In summary, emissions from the following processes must be measured for the LCA of bio-oil sequestration. All CO_2e emissions from the processes should be conservatively estimated. Any unaccounted-for carbon (e.g. lost biomass along the way) is assumed to be emitted as carbon dioxide.

- Emissions from biomass production, including changes from baseline state, if any.

- Emissions from harvesting and transportation of biomass from its source using standardized values for a vehicle type, fuel type and transport distance.

- CO_2-equivalent GHG emissions from bio-oil production, calculated based on the energy consumed in the process (directly when fossil fuels or indirectly when electricity), and any other GHGs created by the process, such as NOx.

- CO_2 emissions from biomass and bio-oil transport, calculated from standardized values for a vehicle type and transport distance.

- CO_2 emissions at the injection site, calculated based on energy usage, energy source standardized emissions values[10], and operating times.

- Bio-oil carbon injected into storage as measured via elemental carbon content (ASTM5291) and bio-oil weight or volume.

- Any fugitive emissions must be deducted from the total net removed carbon dioxide.

Step	Biomass Production	Biomass Harvesting	Biomass Transport	Conversion to bio-oil	Bio-oil	Bio-oil Injection	Bio-oil Storage
Measurement	Modeled via e.g. GREET	Modeled via e.g. GREET	Measured bill of lading, distances	Measured flue stack emissions, fossil fuel use	Measured flue stack emissions, fossil fuel use	Measured energy use	Measured energy use
Frequency	Per feedstock per region	Per feedstock per region	Per load	Per pyrolyzer, continuous flue emissions indicator	Amount with certified truck scale or flow meter, carbon with 3rd party lab per-pyrolyzer-feedstock pair each year	Per injection well	Per formation

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7   https://greet.es.anl.gov/publication-feedstocks-13

8   See table H5 of https://ww2.arb.ca.gov/sites/default/files/classic/fuels/lcfs/iluc_assessment/iluc_analysis.pdf

9   https://greet.es.anl.gov/publication-cclub-manual-r4

10 The CARB regulation has standard emission values for different regions in the US and globally.
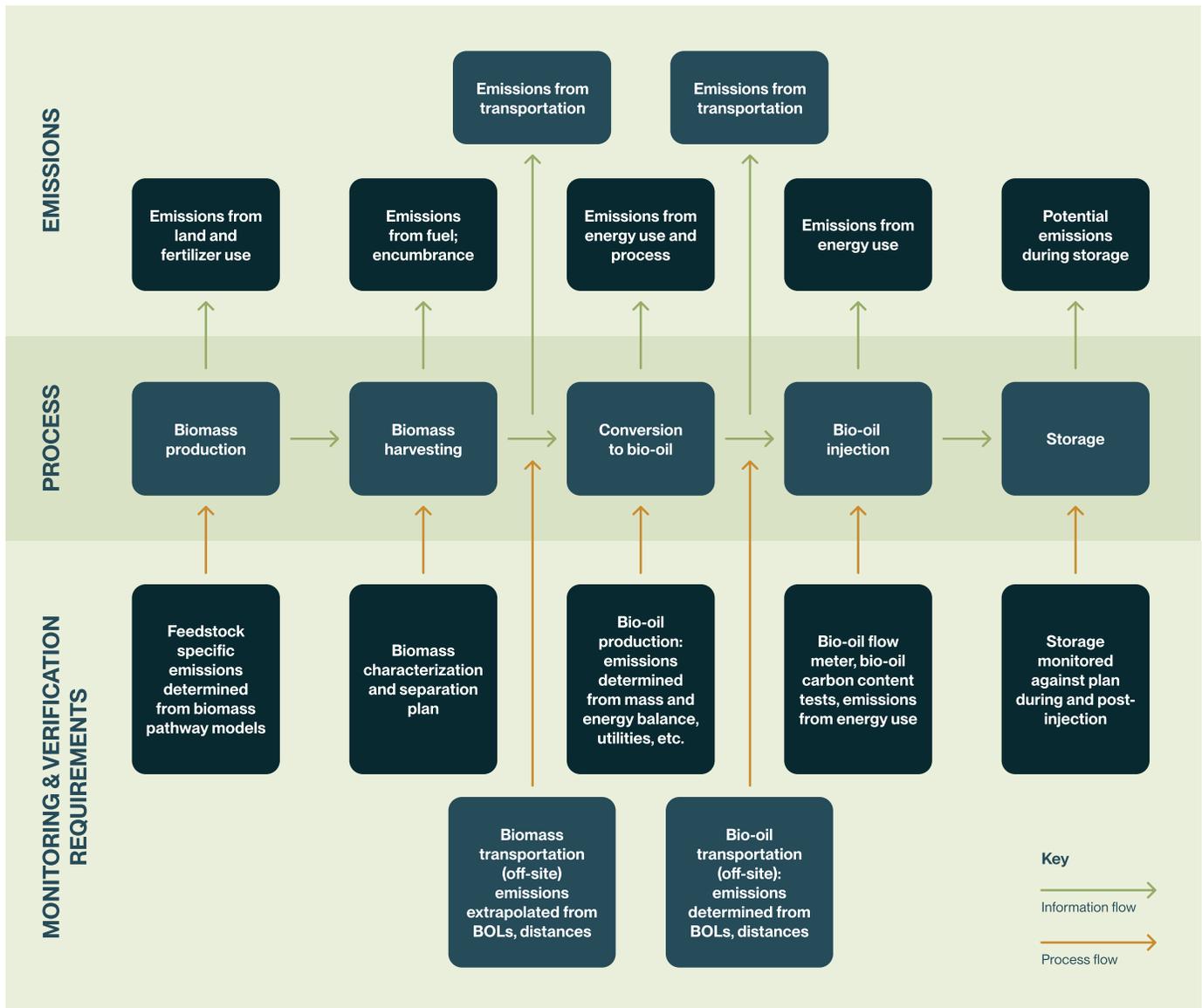
Figure 2 Illustration of a potential LCA for bio-oil sequestration, including likely emissions, monitoring and verification requirements.

Injection Protocol

The fate of any fluids injected into the subsurface is directly a function of the site geology and the sum of well completion history in the injection area. Any project proposing to inject CO_2, bio-oils, or complex biomass-bearing solutions must understand the local geology and wells (both proposed and existing). In the US, the EPA regulates subsurface injection through the underground injection control (UIC) program in order to safeguard drinking water under the Safe Drinking Water Act. That regulatory process requires both an understanding of local geology, proposed wells, and in some cases neighboring wells.

The geological storage of the bio-oil must be assessed, and should be modeled leveraging injection rates, pressures, volumes, and fluid composition and geophysical approaches such as active or passive seismic data, to understand the likely extent of the bio-oil injection. The geochemical compatibility of the bio-oil with the formation must be verified as part of the permitting process through empirical demonstration, e.g. core testing or brine sampling. The injected fluid is likely to undergo an increase in viscosity as it polymerizes—see inset box below. Operators must monitor injection regularly to demonstrate both proper storage of injectate for carbon accounting purposes and ensure safe drinking water compliance.

Consistent with the CCS protocol under the California Low Carbon fuel standard, bio-oil must be injected into a well that is constructed and completed to "prevent the movement of fluids into or between any unauthorized zones".[11] Bio-oil injection wells must be constructed to meet USEPA requirements for Class I, II, or V wells under the Underground Injection Control (UIC) Program, depending on the context for injection. The existing UIC standards specify minimum operating, monitoring, and reporting requirements for such wells.[12]

The monitoring plan should include, but not necessarily be limited to, the following:

- A comprehensive characterization of the sequestration site, including traditional subsurface geologic interpretation using regional geological studies, cores, well logs/seismic data and other reservoir characterization approaches to design the monitoring plan.

- An operational protocol for regular pressure and fluid testing in existing and new wells to address plume migration and fluid conversion. This should include above-injection-zone monitoring or well-bore monitoring for small variations in pressure or temperature in overlying units.

A bio-oil sequestration injection site must be assessed before injection, flowmeter measurements taken as bio-oil is injected[13], and subsequent post-injection monitoring completed to ensure that de minimis fugitive carbon escapes the reservoir during a timeframe that is acceptable to the regulatory body. A performance-based time for post-injection site care (PISC) is recommended, although a 10 year period is likely to be more than sufficient due to the negative buoyancy and viscosity of bio-oils (see inset box).

SUBSURFACE CHANGE OF BIO-OIL

As a non-wetting phase, bio-oils are expected to react very little in the subsurface. Many bio-oils have a higher density than water, which prevents return to the surface. Laboratory tests suggest that viscosity is likely to increase over time in the subsurface, also preventing return. The higher density and viscosity of bio-oils is fundamentally different from either natural hydrocarbons or pure-phase CO_2, which are both buoyand and low-viscosity.

It is possible that some reservoirs contain chemo-autotrophic microbes that could break down a fraction of the bio-oils into CO_2 and methane, which are less dense than water and could be buoyant. Current scientific understanding suggests that the rates of microbial bio-oil conversion would be slow and the volumes very small and thus would not present a material risk. However, conventional monitoring (e.g., above injection zone monitoring or well-bore monitoring) would be sufficient to identify any potential chemosynthetic byproducts and provide a basis for remediation. Under all circumstances, risk of subsurface return would be near zero provided competent well completion in accordance with conventional regulations.

Monitoring and Verification

Monitoring and verification is performed by an independent third party against a monitoring plan. This ensures that the operation is being carried out according to plan and that the calculations of the amount of carbon injected and stored are correctly assessed.

Biomass feedstock sources and transportation distances must be assessed from auditable records. The mass and energy balance at the bio-oil production facility must be calculated using data from actual metered inputs and outputs. Injection of bio-oil must be metered, and the amount of CO2 equivalent credited must be assessed by the verifier over regular time intervals.

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11 https://ww2.arb.ca.gov/sites/default/files/2020-03/CCS_Protocol_Under_LCFS_8-13-18_ada.pdf

12 https://www.epa.gov/uic/underground-injection-control-regulations

13 If all volumes are trucked, it is acceptable to document truck volumes and safe disposal (c.f., no spillage), especially for small volumes. Flow metering would be preferred, especially if the well is in continuous operation.

Metering must be shown to be accurate and reliable[14], and records must be maintained for at least ten years. Monitored sites are observed during and after injection.

Auditing inputs to assess injected carbon must be performed quarterly (and should be performed monthly) and credited once the amount of GHG carbon is verified. Site visits should be required as part of the annual audit cycle.

Reversal Risks

Bio-oils are not buoyant in the subsurface, meaning they pose almost no real risk of reversal. Any minor risks can be best managed through conventional well completion practice for UIC compliance. There is a small chance of microbial alteration of injected bio-oils which must be similarly anticipated and managed. Site selection and well completion have the largest impact on potential risks and should be managed actively in design and operation.

Theoretical reversal risks include migration of the bio-oil out of the geological storage formation or leakage of GHG formed by chemical reactions or anaerobic digestion. The reality of these risks depends on the bio-oil composition (biomass feedstock and conversion process), formation geology, pre-existing microbiota, reservoir operation, and drilling and completion practice. Fundamentally, these risks are minute and can be managed through conventional drilling and completion practice and standard monitoring approaches. This very low (near-zero) risk profile is below the already low risks of CO2 storage, which must manage questions of buoyancy and chemical reactions. The risk of biomethane production is extremely small due to (a) lack of wettability, (b) nutrient limits, and (c) low viscosity (which constrains ability to migrate).

Conclusion

Carbon accounting, monitoring, and verification are well-understood principles in everyday use. Extending the principles to bio-oil production and sequestration can result in the removal of greenhouse gasses from the atmosphere and lay the foundation for the creation of carbon credits from such processes.

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14 Metering should be to industry-standard 95% confidence level or better.

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