Greenhouse Gas and Energy Life Cycle Assessment of Pine Chemicals Derived from Crude Tall Oil and Their Substitutes

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Summary

Pine chemicals are co-products of papermaking that are upgraded into diverse products from inks to adhesives. They can also be utilized for energy purposes. This research investigates the carbon and energy life cycle assessment (LCA) of pine chemicals derived from crude tall oil (CTO). The study goals are to determine the cradle-to-gate carbon and energy footprint for CTO-derived chemicals, compare CTO-derived chemicals to their likely substitutes, and calculate the carbon and energy effects of shifting CTO resources from current chemical production to biodiesel production. The data collected represent 100% of the U.S. and 90% of the European CTO distillation industry for 2011. This analysis is the first industry-level LCA of pine chemicals. The carbon footprint for CTO-derived pine chemical products is 50% lower than the likely mix of alternative products, including hydrocarbon resins for rubber, ink, and adhesive, alkyl succinic anhydride for paper size, and heavy fuel oil for heat. Current and proposed European policies could result in CTO being classified as renewable biomass for energy production, creating incentive to convert CTO into fuel rather than chemicals. The differences in the carbon and energy footprints of utilizing CTO for biodiesel versus chemicals are not meaningful when comparing European CTO biodiesel, which displaces conventional diesel, to European CTO-derived chemicals, which displace the previously discussed substitutes. Therefore, there is no additional carbon or energy benefit that accrues by diverting CTO from current chemical feedstock applications to use for biodiesel production in Europe.

Keywords:
carbon footprint
crude tall oil
industrial ecology
life cycle assessment (LCA)
pine chemicals
pulp and papermaking

Introduction

Pine chemicals, derived from renewable pine trees, are a mature segment of the global chemical industry. Pine chemicals are collected from living trees or pine stumps and logs or are made from co-products of the kraft pulping process: crude tall oil (CTO) and crude sulfate turpentine (CST) (McSweeney et al. 1987). As co-products, CTO and CST are not produced independently of pulp and paper and are therefore constrained resources. These valuable co-products are upgraded into diverse chemical applications, such as adhesives, inks, surfactants, paints, rubber, and coatings. The present-day and historical industrial practices for conversion of CTO to chemicals is well documented (McSweeney et al. 1987; Drew and Propst 1981). Current and proposed European policies could result in CTO being classified as renewable biomass for energy production, creating incentive to convert CTO into fuel rather than the current suite of chemical applications. This research does not include a review of such policies and is intended as a stand-alone scientific analysis of the theoretical environmental impact of shifting CTO usage from chemical applications to biofuel applications.
This study is the first industry-level greenhouse gas (GHG) and energy life cycle assessment (LCA) of pine chemicals derived from CTO. This work is based on a larger unpublished LCA report completed by Franklin Associates, a Division of Eastern Research Group, Inc. (ERG), for the pine chemicals industry (ACC 2013). A full LCA quantifies and characterizes products’ use of energy and materials and the releases to the air, water, and land for each step from raw material extraction through production, use, and end-of-life (EOL) management (ISO 2006). For commodity chemicals, such as pine chemicals, the use phase and EOL management depend upon the chemicals’ specific applications. Therefore, LCAs on commodity materials are typically conducted as cradle-to-gate analyses that cover all steps from raw material extraction through production of the material ready for use (Jiménez-González 2000). The first goal of this study is to determine the cradle-to-gate GHG emissions and energy demand for distillation products of CTO, including tall oil fatty acid (TOFA), tall oil resin (TOR), distilled tall oil (DTO), tall oil pitch, and tall oil heads. Given that the United States and Europe distill the majority of CTO produced in the world, U.S. and European findings are also leveraged to develop LCA results for global CTO distillation products. The second goal of the research is to build upon the cradle-to-gate carbon and energy footprint of pine chemicals to develop carbon and energy footprint comparative analyses between pine chemicals and their most likely substitutes for use in end applications, such as adhesives, inks, rubber, paints, coatings, surfactants, oilfield chemicals, paper size, and fuel. The comparative analysis results are then used to calculate a weighted average carbon and energy footprint for pine chemical products versus the most likely mix of alternatives. The last goal of this study is to determine the possible carbon and energy footprint effects of shifting all CTO resources from the current pine chemical production profile to 100% biofuels production in Europe based on the mix of alternatives that would replace the diverted pine chemicals.

**Methods and Data**

**Cradle-to-Gate Analysis of Crude Tall Oil Pine Chemical Production**

**System Boundaries**

For production of CTO distillation products from co-products of the kraft pulping and recovery processes, six life cycle stages were identified, starting with softwood tree cultivation and harvesting and ending with CTO distillation products ready to be used in the manufacture of products such as adhesives, surfactants, and coatings.

- **Stage 1** (cultivation through transport of pulpwood to pulp and paper mill): This stage starts with the cultivation of pine trees from seedlings and ends at delivery of the raw forestry materials to the pulp and paper mill. The forestry industries in the United States and Europe are mature and stable and the land requirement is not increasing for these industries (USDA Forest Service 2014; Metla 2011). Therefore, no land-use change was considered in this analysis.
- **Stage 2** (kraft pulping): During the kraft pulping process, forestry products from harvesting and the saw mill are transformed into materials ready for the papermaking process. Black liquor soap (BLS) is recovered as a by-product of this process. Based on data from participating pulp companies, the average output by mass from the kraft pulping process is 95% softwood pulp (the primary intended product), 4% BLS, and 1% CST.
- **Stage 3** (BLS transportation): This phase includes transport of the BLS to the acidulation plant. In the United States, BLS may be supplied to acidulation plants by pipeline from the pulp mill they are located near, or BLS may be transported a longer distance through other forms of transportation, such as truck or rail, owing to the fact that not all U.S. pulp and paper mills have their own acidulation plant. In Europe, almost all pulp and paper mills have their own acidulation plant. The few mills that do not have one usually burn their BLS. BLS is transported to some extent, usually between different mills, or with use phase problems or when inventory is too high.
- **Stage 4** (acidulation): After being recovered and taken to the acidulation plant, BLS is reacted with sulfuric acid to produce CTO.
- **Stage 5** (CTO transportation): CTO is then taken from the acidulation plant to a tall oil refinery. CTO may be supplied to distillation plants by pipeline from the acidulation plant they are located near, or CTO may be transported a longer distance through other forms of transportation, given that one acidulation plant does not typically supply enough capacity for a tall oil refinery.
- **Stage 6** (distillation): After being recovered and transported to the tall oil refinery, CTO is distilled in a fractionation column to more valuable intermediate pine chemicals, such as TOR and TOFA. Tall oil heads and pitch are also produced in this process and considered CTO distillation products. Heads and pitch are typically used as fuel for heat rather than in chemical applications.

These system boundaries are illustrated in figure 1. The analysis accounts for transportation requirements between all life cycle stages within the boundaries of this study. The boundaries for this product system end at the CTO distillation plant. Outgoing product transport, final product manufacture, product use, and EOL are excluded from this cradle-to-gate analysis.

**Primary Life Cycle Inventory Data**

Primary data were collected for 100% of the U.S. CTO distillation facilities and a majority (>90%) of European CTO distillation facilities, with detailed information on data coverage provided in tables S11 and S15 in the supporting information available on the Journal’s website. The data collected are representative of operations for the year 2011. These life cycle inventory (LCI) data are aggregated and shown by region in table 1.
Figure 1  System boundaries for the cradle-to-gate analysis of distillation products from CTO. The overall system boundaries are displayed with the green boxes, whereas specific processes or flows are shown within blue boxes. Processes outside the system boundaries are displayed in gray. CTO = crude tall oil.
Table 1  (a) Product information and (b) unit process data, for 1 tonne of crude tall oil distillation product, at average U.S. or average European biorefinery

(a)

| Product information | U.S. | European | Units | Product allocation (%) |
|---------------------|------|----------|-------|------------------------|
| Heads               | 0.066| 0.048    | tonne | 6.6                    |
| Pitch               | 0.16 | 0.27     | tonne | 16                     |
| Tall oil rosin      | 0.34 | 0.27     | tonne | 34                     |
| Tall oil fatty acid | 0.38 | 0.34     | tonne | 38                     |
| Distilled tall oil  | 0.057| 0.072    | tonne | 5.7                    |
| Heads, combusted internally | 0 | 0.032 | tonne | 0 |
| Pitch, combusted internally | 0 | 0.040 | tonne | 0 |
| Distilled tall oil, combusted internally | 0 | 0.010 | tonne | 0 |

(b)

| Unit process data | U.S. | European | Units |
|-------------------|------|----------|-------|
| Avoided product Steam, for chemical processes, at plant | 0 | -61.9 | kg |
| Material inputs | | | |
| Crude tall oil, at acidulation plant/U.S. | 1.03 | 0.14 | tonne |
| Crude tall oil, at acidulation plant/Nordic | 0 | 0.97 | tonne |
| Nitrogen, liquid and gaseous, at plant | 0 | 8.41 | kg |
| Energy inputs | | | |
| Purchased electricity | 117 | 173 | kWh |
| Natural gas, at industrial boiler | 107 | 6.57 | m³ |
| Biomass energy, as purchased steam | 433 | 584 | MJ |
| Bituminous coal, at industrial boiler | 10.6 | 0 | kg |
| Heads, combusted internally | 0 | 0.032 | tonne |
| Pitch, combusted internally | 0 | 0.040 | tonne |
| Distilled tall oil, combusted internally | 0 | 0.010 | tonne |
| Heavy fuel oil, at industrial boiler | 0 | 3.59 | kg |
| Light fuel oil, at industrial boiler | 0 | 0.66 | kg |
| Incoming transport | | | |
| Truck transport of CTO | 71.4 | 148 | tkm |
| Rail transport of CTO | 555 | 81.3 | tkm |
| Pipeline transport of CTO | 0.58 | 0.026 | tkm |
| Ocean freighter transport of CTO | 0 | 1,150 | tkm |
| Barge transport of CTO | 0 | 18.9 | tkm |
| Wastes | | | |
| Loss (wastewater and sludge) | 0.031 | 0.021 | tonne |

Provided to pulp and paper mill, assumed to displace fossil fuel that paper mill would require. Steam fuel mix that is avoided (per kg steam) = 2.6 MJ natural gas and 0.628 MJ heavy fuel oil.

Derived from black liquor and bark. Steam purchased from nearby pulp mill. The energy values are representative of the total biomass energy to produce the steam (with biomass heating values supplied in table S8 in the supporting information on the Web). The boiler efficiency assumed for biomass conversion is approximately 64% (Environmental Defense Fund 1995).

Incoming transport is assumed as one-way. Distances and modes are based on primary data collected from participating facilities (tables S12 and S16 in the supporting information on the Web).

Detailed information on waste treatment was not available and waste is treated as an elementary flow in the model. However, any energy usage (and associated emissions) is included in the overall energy inputs expressed here.

CTO = crude tall oil; kg = kilograms; kWh = kilowatt-hours; m³ = cubic meters; MJ = megajoules; tkm = tonne-kilometers.
Table 2  Product information and unit process data for 1 tonne of crude tall oil, at average U.S. or average European acidulation plant

| Product/process | U.S. | European | Units |
|-----------------|------|----------|-------|
| **Product**     |      |          |       |
| Crude tall oil, at acidulation plant | 1.00 | 1.00 | tonne |
| **Material inputs** |      |          |       |
| Black liquor soap, at pulp mill/U.S. | 1.87 | 0 | tonne |
| Black liquor soap, at pulp mill/Nordic | 0 | 2.00 | tonne |
| Sodium hydroxide, 50% in $H_2O$ | 0.026 | 0.025 | tonne |
| Sulfuric acid, liquid | 0.19 | 0.20 | tonne |
| **Energy inputs** |      |          |       |
| Purchased electricity | 21.8 | 30.6 | kWh |
| Natural gas, at industrial boiler | 7.09 | 0.21 | m$^3$ |
| Biomass energy, as purchased steam$^a$ | 973 | 1,623 | MJ |
| Bituminous coal, at industrial boiler | 12.2 | 0 | kg |
| Heavy fuel oil, at industrial boiler | 0 | 1.71 | kg |
| **Incoming transport$^b$** |      |          |       |
| Truck transport of BLS | 45.5 | 4.50 | tkm |
| Rail transport of BLS | 574 | 0 | tkm |
| Pipeline transport of BLS | 0.76 | 0.97 | tkm |

$^a$Derived from black liquor and bark. Steam purchased from nearby pulp mill. The energy values are representative of the total biomass energy to produce the steam (with biomass heating values supplied in table S8 of the supporting information on the Web). The boiler efficiency assumed for biomass conversion is approximately 64% (Environmental Defense Fund 1995).

$^b$Incoming transport is assumed as one-way. Distances and modes are based on primary data collected from participating facilities (table S10 and table S14 of the supporting information on the Web).

The composition of 1 tonne of average CTO distillation product globally, based on a weighted average of CTO distillation product volumes from participating facilities in the United States and Europe (derived from tables S13, S17, and S18 in the supporting information on the Web), is 0.36 tonne TOFA, 0.31 tonne TOR, 0.20 tonne pitch, 0.063 tonne DTO, and 0.060 tonne heads. The United States distills approximately 57.5% of CTO-derived intermediate products whereas Europe distills 42.5% of the CTO-derived intermediate products, although the mix of outputs varies by region, with a higher output of TOR in the United States and a higher output of pitch in Europe (table S18 in the supporting information on the Web). For the United States, acidulation data were also collected from CTO refining companies that conduct acidulation at the location of the CTO refinery, which represents 37% of the CTO acidulation in the United States in 2011 (table S9 in the supporting information on the Web). European acidulation data were developed for this study based on average European data provided by industry experts from the participating companies. The data developed for acidulation are provided in table 2.

For unit processes for which primary data were not available or compiled for this study, data from credible published sources or licensable databases, specifically the U.S. LCI Database (NREL 2012) and ecoinvent (2010), were used wherever possible in order to maximize transparency (with specific data sources listed in table S1 of the supporting information on the Web). The LCI data for production of U.S. virgin pulpwod, U.S. virgin unbleached softwood kraft pulp mill outputs, and European virgin unbleached softwood kraft pulp mill outputs are presented in tables S3, S4, and S5 in the supporting information on the Web. Geographical considerations for the U.S. and European CTO distillation products are covered in section 4 of the supporting information on the Web.

Comparative Analysis and Diversion to Biodiesel

Pine chemicals are used in a very diverse set of final end products. Rather than addressing specific end products in which pine chemicals are utilized, the comparative results are limited to the content of pine chemicals or pine chemical substitutes in a product. For each unique end product, the comparative analysis excludes elements (input materials or processes) that are not affected by the use of pine chemical or substitute material content (table S19 through table S25 in the supporting information on the Web). For example, the same mass of TOFA and soybean oil can be used in white trim paint interchangeable without affecting the processing impacts of the paint or the type and mass of other paint material inputs (titanium dioxide, white spirits, zirconium napthenate, cobalt napthenate, calcium napthenate, antiskimming agent, and fungicide) (Phillips....
Table 3  CTO-derived pine chemical comparative analysis substitutes by end market

| Pine chemical | End market | Primary substitutes | Substitute factor<sup>b</sup> | Substitute % of market share (U.S.) | Substitute % of market share (Europe) |
|---------------|------------|---------------------|-------------------------------|------------------------------------|---------------------------------------|
| Paper size    | Alkenyl succinic anhydride (ASA) | 1.0 | 90 | 70 |
| Paper size    | Gum rosin<sup>a</sup> | 1.0 | 10 | 30 |
| Rubber        | C5 hydrocarbon resins | 1.0 | 100 | 100 |
| Adhesives     | Gum rosin ester<sup>a</sup> | 1.0 | 20 | 50 |
| Adhesives     | C5 hydrocarbon resins | 1.0 | 80 | 50 |
| Ink           | Acrylic resin | 1.0 | 100 | 100 |
| Oilfield chemicals | Vegetable oils (soybean—food grade) | 1.0 | 100 | 100 |
| Surfactants   | Vegetable oils (soybean—food grade) | 1.0 | 100 | 100 |
| Paints/coatings | Vegetable oils (soybean—food grade) | 1.0 | 100 | 100 |
| Surfactants   | Vegetable oils (soybean—food grade) | 1.0 | 100 | 100 |
| Paints        | Vegetable oils (soybean—food grade) | 1.0 | 100 | 100 |
| Rubber        | C5 hydrocarbon resins | 1.0 | 100 | 100 |
| Fuel          | Heavy fuel oil #6 | 0.91 | 100 | 100 |
| Heads         | Heavy fuel oil #6 | 0.91 | 100 | 100 |

<sup>a</sup>Gum rosin is derived from pine trees, but not from CTO. Therefore, it is considered an alternative to CTO derivatives in this analysis.

<sup>b</sup>Substitution factor = 1 unit of CTO derivatives can be replaced with × units of alternative.

CTO = crude tall oil; TOFA = tall oil fatty acid; DTO = distilled tall oil.

2013). In some cases, the substitution ratio between a CTO-derived end product and its primary substitute may differ. For instance, the substitution ratio between pitch/heads biofuel mix and heavy fuel oil is not 1:1, given that there is some variability in the heating values of these two fuels. Because there may also be differences in EOL carbon emissions of the end products based on whether the materials are fossil derived or bio based, the EOL life cycle stage was included in the analysis where there are known differences between pine chemicals and their alternatives.

This broad material approach was taken to capture as much of the pine chemicals industry as possible. Additional data collection on the process of upgrading TOR to tall oil resin ester (TORE) was required to cover the key adhesives and inks end markets. The LCI data developed for TORE are provided in table S26 (for the United States) and table S27 (for Europe) in the supporting information on the Web. Table 3 displays the investigated pine chemicals, their respective end markets, and the primary substitute per pine chemical in each end market (Morris 2013a). Figure 2 illustrates the system boundaries for the comparative analysis (see the CTO product application route-current global profile) and diversion of CTO from pine chemicals to biodiesel. Because the end applications for CTO derivatives are so diverse, the study scope is not all-inclusive; however, the end markets shown in table 3 represent at least 80% of all uses of pine chemicals globally based on the primary confidential market data provided by participating CTO distillation organizations. Only the primary substitutes for each end application are included. The market share of each substitute or multiple substitutes was scaled up to 100% of the total market in the LCA model. Based on final product formulations provided by participating CTO distillation organizations, the CTO distillation products and their associated substitutes are generally expected to perform equivalently in the relevant end product, as covered in further detail in section 9 in the supporting information on the Web. Therefore, manufacture and use of the final end products were excluded from the analysis, with the exception of fuel use, where combustion emissions were included. The disposal of the end products is based on average U.S. or average European municipal solid waste (MSW) fates, with the exception of fuel, which is combusted and does not enter the MSW stream. Only disposal of the CTO product or CTO product substitute was accounted for (i.e., no other components of the final end product were included in the disposal modeling).

LCI data for the pine chemical substitutes were derived from a number of existing sources. Gum rosin production was calculated based on a confidential report from a company carrying out gum rosin production in China and distributing it to the United States or Europe. Acrylic resin, heavy fuel oil #6, and soybean oil models were developed from existing LCI databases (ecoinvent 2010; NREL 2012). For the substitutes, alkyl succinyl anhydride (ASA) and C5 hydrocarbon resins, there are no existing LCI data, so theoretical process models were developed to estimate LCI data (tables S29 and S31 in the supporting information on the Web). The process model for the production of C5 hydrocarbon resin is based on the Lewis acid catalyzed reaction of dicyclopentadiene followed by washing, steam stripping, extrusion, and flaking to produce the final C5 hydrocarbon resin product (Cheung 2001). The process model for the production...
Figure 2  System boundaries for comparative analysis and diversion of CTO from pine chemicals to biodiesel. The CTO product application route (current global profile) box covers the application boundaries for the comparative analysis. The CTO biodiesel route shows the alternative usage route if CTO is used for biodiesel rather than the current product application route. CTO = crude tall oil.
of ASA is based on the alkylation of maleic anhydride with 1-octadecene (to produce an 18-carbon-alkene–based ASA) followed by separation and stripping to produce the final ASA product (Felthouse et al. 2001; HERTG 2006). The LCI data used for modeling the pine chemical substitutes are covered in detail in section 11 in the supporting information on the Web.

**Crude Tall Oil Diversion to Biodiesel**

This study considers the significant potential for indirect emissions that may be caused by the substitution of other chemicals in the marketplace should CTO be diverted for energy production. Comparisons are often made between the GHG impacts of biofuels and those of their conventional (fossil) alternatives. This study goes one step further to show the broader, system-wide potential GHG impacts of incentivizing one biomass product over another. CTO is increasingly being used to produce biodiesel for transportation fuel, specifically in Europe (European Biofuels Technology Platform 2012). Therefore, this study explored the carbon and energy footprint implications of such a transition. The theoretical GHG and energy effects of CTO usage for pine chemicals versus biodiesel were investigated based on an example case study. To compare CTO usage for biodiesel versus pine chemicals, two specific scenarios were analyzed:

- The CTO product application scenario, which represents the current profile of CTO usage. Rosin ester, TOR, TOFA, DTO, pitch, and heads are produced at a CTO distillation plant, avoiding production and use of substitute products examined in the comparative analysis—hydrocarbon resins, heavy fuel oil, gum rosin, and vegetable oils.
- The CTO biodiesel scenario, in which 100% of the CTO is processed into biodiesel by hydrogenation and avoids the production and combustion of diesel from fossil fuels.

The system boundaries for the comparison of utilizing CTO for pine chemicals versus biodiesel are illustrated in figure 2. The biodiesel pretreatment and hydrogenation process was modeled from publically available LCI data on biodiesel production from crude rapeseed oil in Finland (figure S11 and table S32 in the supporting information on the Web) (IFEU 2006). Because this is a different feedstock than CTO, there is uncertainty surrounding the use of these LCI data for CTO biodiesel, but these are the most relevant LCI data available for the hydrotreatment technology that is anticipated to be used for CTO (UPM 2013). The biodiesel output is anticipated to displace conventional diesel used for passenger vehicles in Europe. The biodiesel does not displace the conventional diesel on a 1:1 mass ratio, given that the heating value of biodiesel is somewhat lower than an equivalent volume of conventional diesel. The displacement ratio of biodiesel to conventional diesel utilized in this study was calculated to be 0.91. The heating values assumed for biodiesel and conventional diesel were 35.8 megajoules per liter (MJ/L) for conventional diesel and 32.6 MJ/L for biodiesel (Argonne National Laboratory 2013).

**Functional Unit**

The functional unit used for reporting cradle-to-gate CTO distillation product results is a weight basis of 1 tonne of average U.S., European, or global CTO distillation product, made up of the average mix of the intermediate products (TOFA, TOR, DTO, heads, and pitch) for the region of interest. For the comparative analysis, the functional unit is 1 tonne of pine chemicals content used in a specific end application or the mass of substitute required to displace 1 tonne of pine chemicals used in the same end application. Last, the functional unit for determining the impact of diverting CTO from pine chemicals to biofuel is utilization of 1 tonne of CTO for production of biodiesel (with displacement of the energy-equivalent amount of conventional diesel) as compared to utilization of 1 tonne of CTO for pine chemical production (with displacement of the most likely mix of pine chemical substitutes). The displacement of alternatives to biodiesel and pine chemicals are considered given that the focus of the biodiesel analysis is the diversion of CTO from chemical usage to biofuel usage.

**Life Cycle Impact Assessment**

The life cycle impact assessment (LCIA) for this study is limited to global warming potential (GWP) (i.e., a carbon footprint) with a 100-year (100a) time horizon (IPCC 2007) and cumulative energy demand (ecoinvent 2010), with energy results reported for both total energy demand and nonrenewable energy demand. Total energy demand includes nonrenewable and renewable energy sources. Nonrenewable energy sources cover fossil-based resources (e.g., coal, crude oil, and natural gas) and uranium for nuclear energy, whereas renewable energy is from natural resources (e.g., biomass, water, sunlight, and wind) that are continuously replenished or that do not become depleted. The energy demand values are tracked from point of extraction, and the higher heating values utilized to determine the energy demand of the primary fuel resources are provided in table S8 in the supporting information on the Web.

**Carbon Storage in Biomass Product Systems**

For products with little or no bio-based content, net flows of biogenic carbon have little effect on the outcomes of the assessment. On the other hand, for products that contain a substantial amount of bio-based materials (e.g., wood pulp) or are derived from bio-based materials (e.g., pine chemicals), attention must be paid to biogenic carbon accounting in order to accurately characterize the flow of GHGs in products and co-products.

In biomass systems, carbon dioxide (CO$_2$) is removed from the atmosphere and incorporated into the material that is harvested from the forest or field. This (biogenic) carbon is stored in the material throughout the life of the product until that product is combusted or degrades, at which point the carbon is released back into the environment. Combustion and degradation releases are predominantly in the form of CO$_2$ and methane (CH$_4$). This study, in alignment with the Intergovernmental Panel on Climate Change (IPCC)
methodology, assumes a net zero impact for biogenic carbon in the form of CO$_2$ emissions, such as CO$_2$ emissions from the combustion of biomass fuels (IPCC 2007). That is, if the removed carbon from the atmosphere is returned to the atmosphere in the same form, the net impact GWP is zero. Impacts associated with the emission of biogenic carbon in the form of CH$_4$ are included given that CH$_4$ was not removed from the atmosphere and its GWP is 25 times that of CO$_2$ when applying the IPCC (2007) 100a LCIA method.

Emissions of biogenic carbon may be released shortly after the end of the product’s life (e.g., if the product is combusted or degrades quickly) or the carbon may be sequestered in a landfill for a long period of time (e.g., hundreds or thousands of years if the product does not decompose quickly). Because the biogenic carbon stored in biomass-derived products in a landfill represents carbon removed from the atmosphere, it is deducted (i.e., has a negative flow) from the total carbon footprint of the product. In this comparative analysis, carbon storage in the CTO distillation products is considered temporary, given that the net carbon storage depends on the fate of the end product in which the distillation product is eventually used. According to the American Chemistry Council (ACC) Pine Chemistry Panel, the landfill decomposition half-life of the products derived from CTO is often short enough that any carbon stored in the product would be returned to the atmosphere within the 100-year assessment period (ACC 2012). Because the use and disposal of the product is not part of this comparative analysis (except for inclusion of combustion emissions for fuel products), and to avoid potential overstating of net long-term storage of biogenic carbon, carbon storage in the CTO distillation products was not included in the baseline assessment. Some carbon may, however, remain stored in the end products with pine chemicals and other bio-derived substitutes that do not decompose. Because detailed modeling of the diverse set of potential end products was not conducted here, this carbon storage was not included in the comparative analysis. Inclusion of EOL carbon storage in the specified pine chemical products would decrease the overall carbon footprint of pine chemicals.

**Allocation**

The two main processes in which allocation was necessary were pulp and distillation. In both cases, allocation was conducted on a mass basis in the baseline scenario (i.e., each kilogram [kg] of useful output from a process is allocated an equivalent share of the process burdens). Because CTO produced from BLS is a useful output from the pulping process (although not the primary intended output product), the base case uses an approach in which BLS is assigned a share of the pulping process burdens. A sensitivity analysis was included in this study calculating results if BLS is treated as a by-product of the kraft pulping process, in which case all of the pulp burdens are assigned to the pulp and none to the BLS. A sensitivity analysis applying economic allocation at the pulp mill was also conducted, in which the process burdens were allocated to the outputs based on the economic value of the output products.

The ratio of economic value of BLS to softwood pulp in the United States is 0.16:1 and in Europe is 0.33:1 (Morris 2013b; PaperAge 2013). Allocation of BLS as a by-product or using an economic approach would decrease the overall carbon and energy footprint of CTO-chemicals. Sections 13 and 14 in the supporting information on the Web covers the methodology and results of these sensitivity analyses.

Allocation of CTO distillation products was necessary because multiple participating facilities could only provide data on a facility level. Products do come off of the fractionation columns at different stages based on boiling points. A typical sequence of how products would come off of a fractionation column is: (1) heads, (2) TOFA, (3) DTO, (4) TOR, and last, (5) pitch. Because all products do not come off of the column at the same stage, an energy allocation is another approach that was considered. However, an energy allocation was not feasible to do in this study because participating facilities were unable to provide the necessary level of detail on operating requirements for the columns within the facilities.

**Results and Discussion**

**Cradle to Gate**

Table 4 shows the baseline carbon footprint results by life cycle stage for the functional unit of 1 tonne of average CTO distillation products for three different regions. Because the United States and Europe distill the majority of CTO produced in the world, U.S. and European findings were also leveraged to develop LCA results for global CTO distillation products. For the United States, the pulping process makes the greatest contribution to the total carbon footprint of U.S. CTO distillation products, followed by the distillation process, forestry activities, and acidulation. For the European system, the pulping process also makes the greatest GHG contribution to the total carbon footprint of CTO distillation products, followed by forestry activities, acidulation, distillation, and CTO transport. The overall carbon footprint, and, specifically, the distillation carbon footprint, is notably lower in Europe than in the United States, primarily because the European system uses more low-carbon fuels (e.g., nuclear, hydro, and biomass), and many plants combust some of their own products (e.g., heads, pitch, and DTO) to use for fuel during processing. Because CTO distillation products are derived from biomass, the CO$_2$ from combustion of these products is considered carbon neutral.

The majority of energy required for the production of CTO distillation products is renewable energy (81% to 86%), including use of biomass as a material feedstock and biomass combusted for energy during processing. Biomass feedstock energy accounts for 33% to 39% of the renewable energy. Whereas total energy demand (nonrenewable and renewable energy) for cradle-to-gate CTO distillation products is higher for Europe than the United States, the nonrenewable energy demand is higher for U.S. products, as presented in table 4. The total energy demand is higher for Europe because many
Table 4  Baseline cradle-to-gate (a) carbon footprint and (b) nonrenewable energy footprint results for 1 tonne of CTO distillation product output by geographical region

(a) Carbon footprint

| Life cycle stage                          | U.S. | Europe | Global |
|------------------------------------------|------|--------|--------|
| Cultivation through pulpwood to mill     | 300  | 148    | 238    |
| Kraft pulping (BLS as co-product)        | 559  | 451    | 515    |
| BLS transportation                       | 16.2 | 2.55   | 10.7   |
| Acidulation                              | 173  | 76.4   | 134    |
| CTO transportation                       | 15.4 | 25.6   | 19.5   |
| Distillation                             | 402  | 36.7   | 254    |
| Total                                    | 1,466| 740    | 1,171  |

(b) Nonrenewable energy footprint

| Life cycle stage                          | U.S. | Europe | Global |
|------------------------------------------|------|--------|--------|
| Cultivation through pulpwood to mill     | 4.49 | 1.74   | 3.38   |
| Kraft pulping (BLS as co-product)        | 6.56 | 9.62   | 7.80   |
| BLS transportation                       | 0.23 | 0.037  | 0.15   |
| Acidulation                              | 1.23 | 1.27   | 1.25   |
| CTO transportation                       | 0.22 | 0.37   | 0.28   |
| Distillation                             | 5.96 | 2.12   | 4.40   |
| Total                                    | 18.7 | 15.2   | 17.3   |

Note: CTO = crude tall oil; BLS = black liquor soap; kg CO$_2$-eq = kilograms carbon dioxide equivalent; GJ = gigajoules.

European plants combust their own products (e.g., pitch, heads, and DTO) for fuel during CTO distillation, which increases the raw material required for production of a net output of 1 tonne of pine chemicals for off-site uses. U.S. facilities do not combust their own products for fuel. Because the European system relies more on biomass energy than the U.S. system, and because the electrical grids serving the plants in Europe have a larger percentage of fuel from renewable sources, the nonrenewable energy demand for cradle-to-gate CTO distillation products is higher in the United States than in Europe.

The baseline results for CTO-derived chemicals include an allocated portion of energy and GHG impacts for upstream forestry and kraft pulping operations, and do not include a credit for storage of biogenic carbon in the pine chemicals during their useful life. Because these modeling choices affect the net energy and carbon footprint results, sensitivity analyses have been run on these assumptions. Specific sensitivity analyses modeled in this study are:

- Treatment of CTO as a by-product of the kraft pulping and recovery process with no burdens upstream of BLS transport to the acidulation plant allocated to the CTO distillation product,
- Inclusion of carbon storage in the pine chemical products, and
- Economic allocation between pulp and BLS at the mill.

All of these sensitivity analysis scenarios result in large reductions in the carbon footprint for cradle-to-gate CTO distillation products. Treating CTO as a by-product (allocating all pulping and forestry burdens to pulp) or applying an economic allocation at the pulp mill also greatly reduces the energy footprint for CTO distillation products. Detailed methodology and results of these sensitivity analyses are provided in sections 13 and 14 of the supporting information on the Web. These sensitivity analyses support the likelihood that the baseline assumptions represent a conservative carbon and energy footprint scenario for pine chemicals.

Comparative Analysis

Figure 3 displays the carbon footprint for global pine chemicals and pine chemical substitutes by end application. The basis of results is 1 tonne of pine chemical input to the end product and the associated amount of substitutes required to displace 1 tonne of the pine chemical. The carbon footprint of pine chemicals is notably lower than that for hydrocarbon resins (C5 resin and acrylic resin) and heavy fuel oil. Globally, gum resin and gum resin ester have larger carbon footprints than TOR and TORE, but not to the same extent as the fossil-derived material. There is not a meaningful difference between the global pine chemical carbon footprints and the soybean oil carbon
Figure 3  Comparative results for (a) carbon footprint for global pine chemicals and global pine chemical substitutes by end application and (b) nonrenewable energy footprint for global pine chemicals and global pine chemical substitutes by end application. CTO-derived pine chemical results are displayed in green, and CTO-derived pine chemical substitute results are displayed in blue. CTO = crude tall oil.
The results for diverting CTO feedstock from pine chemicals to biodiesel (a) carbon footprint (b) nonrenewable energy footprint. The purple delta bar shows the overall change in carbon or energy footprint when shifting the CTO resource. CTO = crude tall oil.

Figure 4

Similar results are observed for the nonrenewable energy analysis (figure 3).

By applying the market share of the end products, weighted average reduction in carbon footprints of pine chemicals compared to their most likely substitute mix can be calculated. The carbon footprints of U.S. pine chemicals are approximately 40% lower than those of their substitutes, the carbon footprints of European pine chemicals are approximately 70% lower, and
the carbon footprints of the weighted global pine chemicals are approximately 50% lower. Similarly, the nonrenewable energy footprint of U.S. pine chemicals is approximately 4% lower than for their substitutes; for European pine chemicals, it is approximately 61% lower, and for weighted global pine chemicals, it is approximately 57% lower.

Crude Tall Oil Diversion to Biodiesel

The results of comparing the carbon and energy footprint of pine chemicals to their most likely substitutes were leveraged to understand the indirect impact of diverting CTO from chemical usage to biofuel production. Because the purpose of this analysis is to understand the impacts of two different options for processing and use of CTO, results are displayed on the functional unit basis of 1 tonne of CTO utilized. This basis differs from the previous comparative results analyses, which are based on 1 tonne of pine chemicals produced.

When examining diversion of CTO from chemical applications to European biofuel applications, two likely routes for sourcing CTO were analyzed:

- CTO sourced from Europe: 50% of the CTO is sourced from an on-site European pulp and paper mill, and the remaining 50% of the CTO is sourced from other mills within Europe. Fifty percent of on-site CTO sourcing is the likely scenario for the case study examined here (UPM 2013).
- CTO globally sourced: 50% of the CTO is sourced from an on-site European pulp and paper mill; of the remaining 50%, 25% is sourced from other mills within Europe and 25% is sourced from the United States. There is no CTO biodiesel industry currently in the United States, so U.S. production of biodiesel from CTO was not considered.

Figure 4 displays the comparative carbon and nonrenewable energy footprint results when diverting the CTO feedstock from pine chemicals to biodiesel for transportation. This study found no meaningful difference in carbon footprint impacts if shifting all CTO use from pine chemicals to biodiesel. This study also found no meaningful difference between the nonrenewable energy footprints or the total energy footprints when CTO is used for pine chemicals versus biodiesel. Therefore, when considering the indirect impact on the pine chemicals’ market, there is no additional carbon or energy benefit that accrues by diverting CTO currently being used as a chemical feedstock to biodiesel production.

Conclusions

This study established the first industry-level pine chemicals carbon and energy footprint. The study met its goals to establish a baseline cradle-to-gate global carbon and energy footprint for CTO distillation products. The research also found that substantial GHG and nonrenewable energy savings are realized when utilizing CTO for chemical applications rather than the most likely mix of substitutes if CTO were not available. This substitute analysis provides a more complete assessment of the impacts of diverting CTO from chemical usage. The pine chemicals industry is vulnerable to policies that could shift CTO away from chemical usage and toward biofuel usage for transportation fuels. The current challenge facing the pine chemical industry is further intensified by the fact that CTO is a co-product of the pulp and paper industry and would not be produced independently of pulp and paper, making it a constrained and limited resource. The study found that differences in the carbon and energy footprints of utilizing CTO for biodiesel versus chemicals are not meaningful when comparing European CTO biodiesel, which displaces conventional diesel, to European CTO-derived chemicals, which displace the previously discussed substitutes. Therefore, there is no additional carbon or energy benefit that accrues by diverting CTO currently being used as a chemical feedstock to biodiesel production.

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**Supporting Information**

Additional Supporting Information may be found in the online version of this article at the publisher’s web site:

**Supporting Information S1**: This supporting information provides detailed information on the data sources utilized in this study, the life cycle inventory data and model description relevant to various phases of the life cycle, discussion of the geographical scope of this study, explanation of energy demand considerations and heating values, and details on sensitivity analyses conducted.