Co-Optimization of Fuels & Engines

Toxicology and Biodegradability of Blendstocks for Mixing Controlled Compression Ignition Combustion

Literature Review of Available Data

November 2020

About the Co-Optimization of Fuels and Engines Initiative

This is one of a series of reports produced as a result of the Co-Optimization of Fuels & Engines (Co-Optima) initiative, a U.S. Department of Energy (DOE)–sponsored effort initiated to simultaneously investigate advanced engine designs and the enabling fuel properties. This first-of-its-kind effort is designed to provide American industry with the scientific underpinnings needed to maximize vehicle performance and efficiency, leverage domestic fuel resources, boost U.S. jobs, and enhance energy security.

Co-Optima brings together DOE’s Office of Energy Efficiency & Renewable Energy (EERE), 9 national laboratories, 13 universities, and more than 20 industry and government stakeholders in a collaboration exploring solutions with potential for near-term improvements to the types of fuels and engines found in most vehicles currently on the road, as well as to the development of revolutionary engine technologies for a longer-term, higher-impact series of solutions.

In addition to the EERE Vehicle Technologies and Bioenergy Technologies Offices, the Co-Optima team includes representatives from the National Renewable Energy Laboratory and Argonne, Idaho, Lawrence Berkeley, Lawrence Livermore, Los Alamos, Oak Ridge, Pacific Northwest, and Sandia National Laboratories. More details on the project—as well as the full series of reports—can be found at www.energy.gov/fuel-engine-co-optimization.

Availability

This report is available electronically at no cost from <http://www.osti.gov/bridge>.

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Report Contributors and Roles

Lead Author

Teresa L. Alleman, National Renewable Energy Laboratory

Contributing Authors

Dennis Smith, Rebecca Brim, and David Barboza, National Renewable Energy Laboratory

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DOE Office of Energy Efficiency and Renewable Energy

- Michael Berube, Acting Deputy Assistant Secretary for Transportation

Bioenergy Technologies Office

- Michael Berube, Acting Director
- Alicia Lindauer, Technology Manager, Bioenergy Analysis & Sustainability

Vehicle Technologies Office

- David Howell, Acting Director
- Gurpreet Singh, Program Manager, Advanced Engine and Fuel Technologies
- Kevin Stork, Technology Manager, Advanced Engine and Fuel Technologies
- Mike Weismiller, Technology Manager, Advanced Engine and Fuel Technologies

National Laboratory Project Management Team

- Robert Wagner (Technical Monitor), Oak Ridge National Laboratory (ORNL)
- Anthe George, Sandia National Laboratories (SNL)
- Dan Gaspar, Pacific Northwest National Laboratory (PNNL)
- Robert McCormick, National Renewable Energy Laboratory (NREL)

This report was reviewed by:

- Cameron Hays, Chemist, National Renewable Energy Laboratory
- Gina Fioroni, Senior Chemist, National Renewable Energy Laboratory

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Abbreviations and Acronyms

4-BH	4-butoxyheptane
5-Et-4-PrNonane	5-ethyl-4-propylnonane
2-MeC17	2-methylheptadecane
2-MeC15	2-methylpentadecane
α -MeNaph	α -methylnaphthalene
BCF	bioconcentration factor
BuCyclohexane	n-butylcyclohexane
CAS	Chemical Abstracts System
CFR	Code of Federal Regulations
Co-Optima	Co-Optimization of Fuels and Engines
DOE	Department of Energy
EPI Suite™	Estimation Programs Interface Suite
HeHexanoate	hexylhexanoate
MCCI	mixing controlled compression ignition
MeDecanoate	methyl decanoate
MeOleate	methyl oleate
MeStearate	methyl stearate
NBB	National Biodiesel Board
NRB	not readily biodegradable
NREL	National Renewable Energy Laboratory
QSAR	quantitative structural activity relationships
RB	readily biodegradable
TEST	Toxicity Estimation Software Tool
wt%	percent by weight

Executive Summary

The goal of the U.S. Department of Energy's Co-Optima project is to develop an understanding of potential biomass-derived blendstocks for use in the transportation sector. This report documents the estimated environmental and toxicological impact of potential bioblendstocks for mixing controlled compression ignition (MCCI) engines. The candidate molecules were: 2-nonanol; n-undecane; 2,6,10-trimethyldodecane; 5-ethyl-4-propylnonane; hexylhexanoate; methyldecanoate; dibutoxymethane; 4-butoxyheptane; dipentylether; renewable diesel; and soy biodiesel. To provide a robust comparison, diesel surrogate molecules were also considered: α -methylnaphthalene; decahydronaphthalene; 2,2,4,4,6,8,8-heptamethylnonane; n-butylcyclohexane; n-hexadecane; tetralin; and n-dodecylbenzene.

The intent of this work was not to provide absolute answers and remove any molecules from consideration, but to provide more robust data for each molecule that can be used in subsequent evaluations. Little literature data was available for many of the molecules, both potential blendstocks and diesel surrogates, so a quantitative structural activity relationship (QSAR) approach was used to provide input into the relevant models.

This assessment included an evaluation of compartment partitioning in the event of an accidental chemical spill, fate and transport indicators, estimated biodegradability, and human and environmental toxicology. The higher molecular weight and longer hydrocarbon chain lengths of these MCCI molecules reduce water solubility and mobility. Generally, the oxygenated molecules improved biodegradability metrics. The hydrocarbons farnesane and 5-Et-4-PrNonane are not predicted to be biodegradable.

Human acute toxicity was found to be slightly to non-toxic for the MCCI blendstocks and the diesel surrogates. 2-Nonanol, undecane, MeDecanoate, dibutoxymethane, and dipentylether were likely developmental toxicants. Although poorly water soluble, all the compounds, whether Co-Optima blendstocks or diesel surrogates, showed significant toxicity to *D. magna*. The oxygenated blendstocks were less likely to bioaccumulate than the non-oxygenated blendstocks, which behaved similar to the diesel surrogates.

Overall, this predicted analysis showed that the MCCI blendstocks are very similar to their diesel counterparts. No significant showstoppers were found that would indicate concern moving forward with additional research into these potential fuels. The results presented were based solely on predictive models and serve to provide information going forward for continued evaluation of these molecules.

1. Background

In its first three years, The U.S. Department of Energy's (DOE's) Co-Optimization of Fuels and Engines (Co-Optima) project mainly focused on potential improvement for spark-ignited light-duty engines. That work examined a wide range of fuels necessary to optimize light-duty, boosted spark-ignited engines. These optimizations include higher knock resistance, higher compression ratio, turbocharging, engine downsizing and lower speed operation (Stein et al. 2013; Anderson et al. 2014; Chow et al. 2014; Leone et al. 2014; Speth et al. 2014; Leone et al. 2015). The detailed screening approach to physical properties has been well documented (McCormick et al. 2017; Farrell et al. 2018a; Farrell et al. 2018b). Our previous work analyzed additional parameters, including the biodegradability and toxicology of the six most promising gasoline-range blendstocks (Alleman and Smith 2019). That work found little potential environmental concern for the proposed blendstocks based on available literature of the pure compounds.

The next phase of the Co-Optima project considers potential blendstocks for mixing controlled compression-ignition (MCCI) engines. The identification and screening of potential blendstocks followed a similar three-tiered screening approach. The tier one screening identified potential molecules that could be used as a fuel and met required properties for use in diesel engines. This smaller pool of molecules in the second-tier screening identified properties of blends produced with diesel fuel or a diesel fuel surrogate (Fioroni et al. 2019).

Similar to the screening for the light-duty blendstocks, a high-level evaluation was conducted for toxicology and biodegradability. Any potential molecules with an Occupational Safety and Health Administration category 1 or 2 for acute toxicity, carcinogenicity, and/or reproductive toxicity were eliminated from consideration. Potential molecules also had to meet key diesel fuel safety and handling parameters, such as flash point. Fioroni's 2019 work included an initial assessment of anaerobic biodegradability, showing poor responses from several potential MCCI molecules. This work will expand on that initial assessment and use additional tools to more completely evaluate the toxicity and biodegradability of the potential MCCI blendstocks under Co-Optima.

2. Introduction

Gasoline fuel toxicity, particularly due to additives such as tetra-ethyl lead and methyl tert-butyl ether, has been well documented. (42 USC Title 42 Chap 85, Subchap II Part A, Sec 7545; Bevan et al. 1997a; Bevan et al. 1997b; Bird et al. 1997; Daughtrey et al. 1997; Lington et al. 1997; McKee et al. 1990; Miller et al. 1997). In addition to the toxicity of the fuel, toxicity from combustion emissions are also a significant concern (examples include Seagrave et al. 2002; Graham et al. 2008; Karavalakis et al. 2012; von Stackelberg et al. 2013). Similar concerns exist for diesel fuel; acute and chronic exposure to diesel fuel may lead to health problems (Chilcot undated; Risher and Rhodes 1995). Fuel spills may cause harm due to large volumes of chemicals being quickly released into the environment. Unlike gasoline, diesel fuel and its components are less volatile and may not evaporate as readily, leading to different exposure routes in the event of a spill (Department of Ecology 2019).

As discussed in our previous work, the intent of this study is to examine the impact of an accidental environmental release of various pure components being considered as bioblendstocks for MCCI (Alleman and Smith, 2019). The examination of toxicity of fuels and blendstocks spans a wide range of systems, including soil, marine organisms, microbes, and the atmosphere. The goal of the study is to provide additional data for these blendstocks to support further evaluation of their potential to be used as fuels.

The addition of novel blendstocks to diesel fuels face different regulatory hurdles than adding blendstocks to gasoline. Unlike gasoline, there is no “substantially similar” rule for diesel fuel (Federal Register Vol. 84 No. 111, Monday, June 10, 2019). New diesel fuels and additives must be registered with the U.S. Environmental Protection Agency (EPA) and satisfy the provisions of 40 Code of Federal Regulations (CFR) Part 79. Under Part 79, new diesel fuels/additives are classified into three main categories: baseline, non-baseline, and atypical. Baseline diesel fuels/additives have only the elements carbon, hydrogen, nitrogen, sulfur, and oxygen (C, H, N, S¹, and O, respectively); meet ASTM International specification ASTM D975-93; have oxygen content below 1.0 weight percent (wt%); and are derived from petroleum, heavy oil, coal, tar sands, or oil sands. Non-baseline fuels/additives may contain more than 1.0 wt% oxygen and may be derived from different feedstocks than those allowed in the baseline diesel category. The non-baseline diesel group provides further detail if the additive/fuel is an alcohol or ether and provides a separate group for alkyl nitrates, nitro-compounds, nitroso-compounds, peroxides, furans, and alkyl esters from plant or animal origin. Non-baseline diesel fuel/additives may also be derived from shale, used oil, plastic, and recycled petroleum products. Atypical fuels and additives contain other elements besides C, H, N, S, and O.

One of the critical objectives of Co-Optima is to identify blendstocks derived from biomass resources with fit for purpose fuel properties. The potential blendstocks listed in Table 1 are clearly non-baseline due to being derived from biomass. Three of the potential blendstocks —n-undecane; 2,6,10-trimethyldodecane; and 5-ethyl-4-propylnonane—may be already present in diesel fuel in small quantities. The production of these chemicals from biomass would render them non-baseline, in spite of their likely presence in conventional (petroleum-derived) diesel fuel.

The work under Co-Optima will stop well short of submitting data and completing fuel registration; however, it should be noted that 2,6,10-trimethyldodecane (farnesane) has completed the Part 79 registration under the small business provisions (Protection of the Environment 2017). The National Biodiesel Board completed fuel registration for biodiesel in 1997. The regulations allow for group registration, for manufacturers of similar fuels, and National Biodiesel Board member companies, after completing the appropriate paperwork, will be registered with EPA (EPA 2007).

All of the candidate blendstocks contain only C, H, and O and have diesel-like properties (flash point, cloud point, distillation, etc. [Fioroni 2019]). Table 1 lists the potential blendstocks along with several diesel surrogate compounds for comparison. Soy biodiesel and renewable diesel are complex mixtures and representative compounds have been identified and used in this analysis.

¹ 40 CFR Part 80 limits sulfur content to 0.05 wt% in diesel fuel. This limit was further reduced through direct final rule (Federal Register Vol. 66, No. 12, Thursday, January 18, 2001.)

Table 1. Co-Optima MCCI blendstocks

Chemical	CAS#	Shorthand ID	Notes
2-nonanol	628-99-9		Co-Optima blendstock
n-undecane	1120-21-4	Undecane	Co-Optima blendstock
2,6,10-trimethyldodecane	3891-98-3	Farnesane	Co-Optima blendstock
5-ethyl-4-propylnonane	53291-73-9 ^a	5-Et-4-PrNonane	Co-Optima blendstock
Hexylhexanoate	6378-65-0	HeHexanoate	Co-Optima blendstock
Methyldecanoate	110-42-9	MeDecanoate	Co-Optima blendstock
Dibutoxymethane	2568-90-3		
4-butoxyheptane	N/A	4-BH	Co-Optima blendstock
Dipentylether	693-65-2		Co-Optima blendstock
Renewable diesel	N/A		Co-Optima blendstock
2-methylpentadecane	1560-93-6	2-MeC15	Renewable diesel surrogate
2-methylheptadecane	1560-89-0	2-MeC17	Renewable diesel surrogate
Soy biodiesel	67784-80-9		Co-Optima blendstock
Methyl stearate	112-61-8	MeStearate	Biodiesel surrogate
Methyl oleate	112-62-9	MeOleate	Biodiesel surrogate
α -methylnaphthalene	90-12-0	α -MeNaph	Diesel surrogate
decahydronaphthalene	493-02-7	Transdecalin	Diesel surrogate
2,2,4,4,6,8,8-heptamethylnonane	4390-04-9	Isocetane	Diesel surrogate
n-butylcyclohexane	1678-93-9	BuCyclohexane	Diesel surrogate
n-hexadecane	544-76-3	Cetane	Diesel surrogate
Tetralin	119-64-2		Diesel surrogate
n-dodecylbenzene	123-01-3	Dodecylbenzene	Diesel surrogate

CAS: Chemical Abstracts System

3. Methods and Results

3.1. Overall Approach

The intent of this work is to provide decision makers with robust analysis to support further evaluations of these potential blendstocks. Many of the diesel-like compounds have very little literature data available to aid in developing relative comparisons. The approach for the MCCI compounds relies heavily on quantitative structure activity relationships (QSARs) to provide inputs to standard models to predict environmental and toxicological outcomes. Because a paucity of data on diesel-like molecules exists it becomes necessary to rely on models and estimation to gauge relative impact.

The application of the QSAR approach to broad categories of toxicity has been well documented, including the pros, cons, and limitations (Cardamone et al. undated; Schultz et al. 2003; Cherkasov et al. 2014). The basic QSAR approach starts with the quantitative activity relationships for known chemicals, either chemical or biological. Examples of quantitative activities are boiling point, water solubility, partition coefficients, biodegradability, rat LD₅₀, and *D. magna* LC₅₀.² These response variables are matched to the predictor variables—chemical compositional fragments. The experimental library for many known chemicals (identified by their functional fragments) and measured experimental activities (both chemical and biological) are then used to mathematically predict the chemical and biological response activities of new chemicals based on their compositional fragments. The QSAR approach can be applied regressively to give predicted numerical responses for the new chemical or as classification models with descriptive categorical responses. It is assumed that an additive approach using the relative contribution of each fragment can be applied to estimate the overall impact of the compound of interest.

One of the more significant assumptions in this approach is that training sets, which may be composed of more simple molecules, can be used to predict larger and more complex molecules. In essence, the model assumes homologous series of fragments are well behaved and can be predicted using mathematical tools. As the majority of blendstocks included in this paper do not have supporting experimental data, either chemical or biological, with which to model toxicity and environmental impacts, all blendstocks will be treated by the QSAR approach and the resulting predicted activities or properties will be incorporated into models presented within the results.

This study will use the QSAR approach to compare the relative environmental impact of the potential bioblendstocks with the diesel surrogate molecules. The analyses presented here are relative and meant to inform, rather than make strict recommendations for future activities with these blendstocks.

3.2. Compartment Modeling

Each molecule was assessed to determine which compartment(s) would be most significantly impacted in the event of an accidental release to the environment. The key compartments are air, soil, water, sediment, and suspended sediment. The analysis is based on the work of Mackay (2001) and analyzed using the software program: Level I, Fugacity-Based Environmental Equilibrium Partitioning Model (Trent University 2004). The same assumptions—homogeneous compartments and all compartments are in equilibrium—apply and are discussed in more detail in our previous work (Alleman and Smith 2019). Graphical representation of the compartments for each compound are given in the appendix.

Table 2 shows where each chemical would partition, by percentage, based on this analysis. Data for fish and aerosols are not shown as our analysis showed only trace levels for these compartments. The potential bioblendstocks do not exhibit partitioning trends highly different from the diesel surrogates with the majority residing in the air and/or soil compartments.

² *Daphnia magna* lethal concentration 50 (LC₅₀) represents that concentration in water that kills half of the *D. magna* (a water flea) in 48 hours. It is a common ecological screening test. The risk index is an order of magnitude categorization test whose results are generated by TEST (EPA 2016c) to compare the chemicals. For perspective, the LC₅₀ for n-undecane for *D. magna* is one order of magnitude lower (more toxic) than that of 2-nonanol.

Compared to the light-duty Co-Optima molecules, mobility into the water compartment is less significant for all the bioblendstocks except for 2-nonanol.

Table 2. Percentage of Compounds Partitioning in Various Environmental Compartments

Compound	Air, %	Soil, %	Water, %	Sediment, %	Suspended Sediment, %
2-nonanol	26.9	42.9	29.2	0.954	0.0298
Undecane	95.4	4.51	0.00927	0.100	0.00313
Farnesane	85.7	14.0	trace	0.311	0.00971
5-Et-4-PrNonane	88.7	11.0	0.00106	0.245	0.00766
HeHexanoate	48.4	49.6	0.908	1.10	0.0344
MeDecanoate	71.6	26.6	1.17	0.592	0.0185
Dibutoxymethane	92.8	2.38	4.78	0.0529	0.00165
4-BH	92.6	6.91	0.313	0.153	0.00480
Dipentylether	92.9	6.27	0.708	0.139	0.00435
Renewable diesel					
2-MeC15	46.1	52.6	trace	1.17	0.0366
2-MeC17	10.0	88.0	trace	1.95	0.0611
Soy biodiesel					
MeStearate	0.140	97.6	trace	2.17	0.0678
MeOleate	0.637	97.1	0.00389	2.16	0.0674
α -MeNaph	81.8	15.5	2.36	0.344	0.0108
Transdecalin	96.9	2.94	0.0663	0.0654	0.00204
Isocetane	93.5	6.34	trace	0.141	0.00440
BuCyclohexane	97.5	2.42	0.0232	0.0537	0.00168
Cetane	24.3	74.0	trace	1.64	0.0514
Tetralin	70.9	20.9	7.65	0.465	0.0145
Dodecylbenzene	0.695	97.1	trace	2.16	0.0674

3.3. Fate and Transport Indicators

The physical and chemical properties of these blendstocks and surrogates are critical to further describing their potential environmental impact. Table 3 begins to incorporate estimated physical properties from EPISuite. For a portion of the compounds, physical data are available, such as in the NREL Fuel Property Database (NREL 2020); however, for consistency, all values are estimated to provide “apples to apples” comparison for this analysis. Vapor pressure is an indication of the volatility of a compound and is related to how much of a compound would partition into the air compartment.

An estimate of how likely a chemical is to persist in the soil is given by the soil/sediment-to-water partition coefficient. Higher values indicate the compound will remain in the soil and not migrate into water. In addition to the partition coefficient, the predicted water solubility and aerobic biodegradability are important transport indicators. A relative mobility descriptor (MD) was developed by Ford and Gurba (1984) and is described by equation (1). The mobility descriptor is qualitatively ranked from “extremely mobile” to “very immobile.”

$$MD = \log \frac{\text{Water Solubility} \times \text{Vapor Pressure}}{\text{Soil Sediment Partition}} \quad (1)$$

Table 3. Common Fate and Transport Indicators

Chemical	Vapor Pressure, mmHg @ 25C	Water Solubility, mg/L@25C unless otherwise noted ^b	Soil/Sediment to Water Partition Coefficient ^b	Relative Mobility Descriptor	Predicted Biodegradability ^c (U.S. National Library of Medicine)
2-nonanol	0.109 ^a	460 ^a	197	Slightly mobile	No information
Undecane	0.629 ^a	0.257 ^a	95,800	Slightly immobile	Readily biodegradable
Farnesane	0.130	0.00442	3,160,000	Slightly immobile	No information
5-Et-4-PrNonane	0.187	0.0119	1,370,000	Slightly immobile	No information
HeHexanoate	0.0348	3.52	3,230	Slightly mobile	No information
MeDecanoate	0.107 ^a	8.79 ^a	1,990	Slightly mobile	Rapidly biodegradable
Dibutoxymethane	1.37	305	184	Very mobile	No information
4-BH	0.672	10.2	1,880	Slightly mobile	No information
Dipentylether	0.830*	27.0	1,110	Slightly mobile	No information
Renewable diesel					
2-MeC15	0.0182	0.00106	11,400,000	Very immobile	No information
2-MeC17	0.00205	0.000108	80,600,000	Very immobile	No information
Soy biodiesel					

Chemical	Vapor Pressure, mmHg @ 25C	Water Solubility, mg/L@25C unless otherwise noted ^b	Soil/Sediment to Water Partition Coefficient ^b	Relative Mobility Descriptor	Predicted Biodegradability ^c (U.S. National Library of Medicine)
MeStearate	0.0000328 ^a	0.000927	301,000	Very immobile	Partially biodegradable
MeOleate	0.000115 ^a	0.00559	95,500	Very immobile	Rapidly biodegradable
α -MeNaph	0.0368 ^a	40.6 ^a	2,280	Slightly mobile	Not biodegradable
Transdecalin	0.942 ^a	2.40 ^a	12,000	Slightly mobile	Not biodegradable
Isocetane	0.271	0.00205	5,760,000	Very immobile	No information
BuCyclohexane	1.27 ^a	1.14	25,100	Slightly mobile	No information
Cetane	0.00696 ^a	0.000919 ^a	13,100,000	Very immobile	Biodegradable
Tetralin	0.246 ^a	94.3 ^a	1,070	Slightly mobile	Limited biodegradation
Dodecylbenzene	0.000436 ^a	0.00102 ^a	32,100,000	Very immobile	Biodegradable

^a Though an experimental value is available, the predicted value from EPI Suite model was used to maintain comparative consistency with other compounds.

^b (Koc by Kow method) L/kg

^c U.S. National Library of Medicine

By considering these variables together, a picture begins to form of the transport fate of these compounds. None of the diesel surrogate molecules or the Co-Optima blendstocks has significant water solubility or vapor pressure, especially compared to our previous analysis of light-duty Co-Optima blendstocks. For the diesel surrogate molecules, isocetane, cetane, and dodecylbenzene have the highest soil/sediment-to-water partition coefficients. Alpha-methylnaphthalene, n-butylcyclohexane, transdecalin, and tetralin have limited predicted biodegradability and some mobility between the soil and water phase.

In comparison, the proposed Co-Optima blendstocks cover a range of potential scenarios. The non-oxygenated compounds (undecane, farnesane, 5-Et-4-PrNonane, 2MeC15, and 2MeC17) are predicted to behave more like the diesel surrogate compounds, with higher soil/sediment-to-water partition coefficients and lower water solubilities. The oxygen-containing compounds (2-nonanol, HeHexanoate, MeDecanoate, dibutoxymethane, 4-BH, dipentylether, MeStearate, and MeOleate) have relatively higher water solubility and lower partition coefficients.

3.4. EPI Suite™ Screening

One common and readily available method for estimating biodegradability is through the Estimation Program Interface Suite™ (EPI Suite). For the Co-Optima MCCI molecules, the estimates of biodegradability are particularly important, as little measured data exist (see Table 3). In Table 4, two estimates of biodegradability are provided: aerobic and anaerobic.

Table 4. EPI Suite Output for Aerobic and Anaerobic Biodegradability

Chemical	Bayesian Battery Approach Result for Aerobic Biodegradability	BIOWIN7 Result for Anaerobic Biodegradability	Water solubility, mg/L@25 °C ^a
2-nonanol	RB	0.482	460 ^b
Undecane	RB	0.275	0.257 ^b
Farnesane	NRB	0.123	0.00442
5-Et-4-PrNonane	NRB	0.0763	0.0119
HeHexanoate	RB	0.447	3.52
MeDecanoate	RB	0.739	8.79 ^b
Dibutoxymethane	RB	-0.291	305
4-BH	RB	0.0385	10.2
Dipentylether	RB	-0.0078	27.0
Renewable diesel			
2-MeC15	RB	0.426	0.00106
2-MeC17	RB	0.478	0.000108
Soy biodiesel			
MeStearate	RB	0.947	0.000927
MeOleate	RB	0.748	0.00559
α -MeNaph	NRB	-0.204	40.6 ^b
Transdecalin	NRB	-0.0451	2.40 ^b
Isocetane	NRB	-0.971	0.00205
BuCyclohexane	RB	-0.0439	1.14
Cetane	RB	0.405	0.000919 ^b
Tetralin	NRB	-0.0292	94.3 ^b
Dodecylbenzene	NRB	0.318	0.00102 ^b

^a EPI Suite^b Though an experimental value is available, the predicted value from the EPI Suite model was used to maintain comparative consistency with other compounds.

The Co-Optima blendstocks are predicted to be readily aerobically biodegradable, with the exception of the farnesane and 5-Et-4-PrNonane. In contrast, the diesel surrogate molecules are not typically aerobically biodegradable, with the exception of BuCyclohexane and cetane. The likely aerobic biodegradability of the Co-Optima blendstocks may become a positive metric for future consideration, as it likely indicates reduced environmental impact compared to conventional fuels.

Only the long-chain esters (MeOleate, MeStearate, MeDecanoate) have predicted anaerobic degradability. HeHexanoate, 2-nonanol, and the renewable diesel surrogate molecules are

borderline, based on the model predictions. In contrast, the diesel surrogate molecules, with the exception of cetane, are not predicted to be anaerobically biodegradable.

3.5. Human Exposure and Toxicology

Another avenue of ecological concern is the potential for human exposure and risk. Table 5 lists common human exposure and toxicological indicators, including acute toxicity (short-term single dose toxicity), developmental toxicity (chemicals that may cause developmental delays in human growth), and chronic toxicity (long-term cumulative toxicity). It should be noted that these indicators were derived from QSAR models and are based heavily on extrapolation of microbial and/or animal systems to human beings. The results tabulated below should be used as rough indicators of human health impacts, rather than strict metrics.

None of the Co-Optima blendstocks nor the diesel surrogates are predicted to exhibit notable acute human toxicity or Ames mutagenicity. Five of the Co-Optima blendstocks exhibited evidence of developmental toxicity (2-nonanol, undecane, MeDecanoate, dibutoxymethane, and dipentylether). Of the diesel surrogates, BuCyclohexane, cetane, and dodecylbenzene also exhibited evidence of developmental toxicity. Based on this predicted metric, the Co-Optima blendstocks do not increase toxicity when blended with diesel fuel.

Farnesane and 5-Et-4-PrNonane have slightly higher predicted chronic toxicity ratings than the other Co-Optima blendstocks. The mid-range levels of these compounds are on par with several of the diesel surrogates, such as transdecalin, isocetane, BuCyclohexane and cetane. The remaining diesel surrogates were found to have a high predicted chronic toxicity.

Table 5. Human Exposure and Toxicology Results

Chemical	Human Acute Toxicity Category ^a	Developmental Toxicity Category ^b	Ames Mutagenicity Assay ^b	Chronic Toxicity Ranking, 1 (high) to 5 (low)
2-nonanol	Slightly toxic	Toxicant	Negative	5
Undecane	Practically non-toxic	Toxicant	Negative	4
Farnesane	Practically non-toxic	Non-toxicant	Negative	3
5-Et-4-PrNonane	Practically non-toxic	Non-toxicant	Negative	3
HeHexanoate	Practically non-toxic	Non-toxicant	Negative	5
MeDecanoate	Slightly toxic	Toxicant	Negative	5
Dibutoxymethane	Slightly toxic	Toxicant	Negative	
4-BH	Slightly toxic	Non-toxicant	Negative	5
Dipentylether	Practically non-toxic	Toxicant	Negative	5
Renewable diesel				
2-MeC15	Practically non-toxic	Non-toxicant	Negative	4
2-MeC17	Practically non-toxic	Non-toxicant	Negative	4
Soy biodiesel				

Chemical	Human Acute Toxicity Category ^a	Developmental Toxicity Category ^b	Ames Mutagenicity Assay ^b	Chronic Toxicity Ranking, 1 (high) to 5 (low)
MeStearate	Practically non-toxic	Non-toxicant	Negative	5
MeOleate	Practically non-toxic	Non-toxicant	Negative	5
α -MeNaph	Slightly toxic	Non-toxicant	Negative	1
Transdecalin	Practically non-toxic	Non-toxicant	Negative	3
Isocetane	Practically non-toxic	Non-toxicant	Negative	3
BuCyclohexane	Practically non-toxic	Toxicant	Negative	3
Cetane	Practically non-toxic	Toxicant	Negative	4
Tetralin	Slightly toxic	Non-toxicant	Negative	1
Dodecylbenzene	Practically non-toxic	Toxicant	Negative	1

^a Based on categorization used in the EPA pesticide registration program. Acute toxicity data from the public domain (predicted median lethal dose or LD₅₀ given by TEST) were compared to the EPA's categorization scheme in 40 CFR 152.62 (EPA 2018b).

^b Based on the structural activity relationships developed using EPA's Toxicity Estimation Software Tool (TEST) (EPA 2016c). These are derived from QSAR models, which are predictors of biological activity based on physio-chemical properties or theoretical molecular descriptors of chemicals. These results should be used as indicators and not necessarily as predictors of biological activity. The database from which these results were extrapolated is nearly all animal or microbial systems, and the administer dosages may not be reflective of the exposure humans would likely receive.

3.6. Ecological Exposure

Beyond human health impacts, ecological impact is also an important consideration for novel blendstocks. Common ecological indicators are listed in Table 6 and include the acute risk index to *Daphnia magna*, bioconcentration factor (BCF), and potential to bioaccumulate. Similar to the other metrics provided in this report, these results are based on QSAR estimations.

All the Co-Optima blendstocks and the diesel surrogates have significant predicted toxicity to *D. magna*. Each numeric increment in Table 6 represents roughly an order of magnitude more toxicity, so a compound with a “2” is one order of magnitude less toxic than a compound with a “1.” With the exception of 2-nonanol, dibutoxymethane, 4-BH, and dipentylether, which are rated “2,” the other Co-Optima blendstocks and all the diesel surrogates are rated a “1.”

Once chemicals enter into microscopic species, the concern about bioaccumulation becomes relevant. These microscopic species are the beginning of the food chain, leading to potential concentration of chemicals in tissues of higher species. The BCF and potential to persist and bioaccumulate reveal similar information for these compounds. Of the potential blendstocks, only the non-oxygenated hydrocarbons exhibit moderate potential to bioaccumulate (undecane, farnesane, 5-Et-4-PrNonane, 2-MeC15, and 2MeC17). The oxygenated compounds have a low potential to bioaccumulate. As expected, the non-oxygenated diesel surrogates also have at least moderate potential to bioaccumulate as well.

Table 6. Ecological Exposure Results

Chemical	Ecological Acute Risk Index <i>Daphnia magna</i> ^a , 1 (High) to 5 (Low)	Bioconcentration Factor (BCF) ^b	Persistence and Potential to Bioaccumulate Category ^c
2-nonanol	2	67.07	Low
Undecane	1	619.99	Moderate
Farnesane	1	805.69	Moderate
5-Et-4-PrNonane	1	990.56	Moderate
HeHexanoate	1	59.31	Low
MeDecanoate	1	81	Low
Dibutoxymethane	2	18.05	Low
4-BH	2	65.53	Low
Dipentylether	2	44.14	Low
Renewable diesel			
2-MeC15	1	316.17	Moderate
2-MeC17	1	363.08	Moderate
Soy biodiesel			
MeStearate	1	49.43	Low
MeOleate	1	77.58	Low
α -MeNaph	1	255.84	Moderate
Transdecalin	1	786.13 ^d	Moderate
Isocetane	1	2,355.19 ^d	High
BuCyclohexane	1	987.81	Moderate
Cetane	1	422.42 ^d	Moderate
Tetralin	1	265.86 ^d	Moderate
Dodecylbenzene	1	284.93	Moderate

^a *Daphnia magna* lethal concentration (LC₅₀) represents that concentration in water that kills half (50%) of the *D. magna* (a water flea) in 48 hours. It is a common ecological screening test. The risk index is an order of magnitude categorization test whose results are generated by TEST (EPA 2016c) to compare the chemicals. For perspective, the LC₅₀ for n-undecane for *D. magna* is one order of magnitude lower (more toxic) than that of 2-nonanol.

^b The BCF is the ratio of the concentration of a chemical in biotic tissue to the concentration in an exposure medium: $BCF = C_{biota}/C_{water}$. There are numerous sources of BCFs in the public domain. These were derived with TEST (EPA 2016c) for consistency.

^c Categorization comes from EPA (2018d). For context, n-undecane has a BCF of 620 and would be categorized as having an “moderate” potential to bioaccumulate.

^d Though experimental value is available, the predicted value from EPA TEST was used to maintain comparative consistency with other compounds.

4. Discussion

The framework provided here, based solely on QSARs to develop model estimates, outlines the potential environmental and toxicological impact of the Co-Optima blendstocks in comparison to several diesel surrogate compounds. The intent of the framework is to provide additional data for decision makers when considering the potential for utilization and continued research into these blendstocks. The results presented are not meant to be absolute, but rather used in conjunction with other available data.

Overall, the Co-Optima blendstocks are predicted to behave no worse than the diesel surrogate compounds. The compartmental modeling shows very similar predicted behavior of the Co-Optima blendstocks and the diesel surrogates with partitioning between the air and soil compartments. The exception is 2-nonanol, which exhibited notable partitioning into water.

Some differences in water solubility and mobility can be derived from the models. The differences are very small, comparatively, for these diesel-boiling range compounds, particularly when compared to the gasoline range compounds found in Alleman and Smith (2019). The larger molecular size and lower volatility of the MCCI Co-Optima blendstocks result in limited water solubility and mobility, especially over to the SI Co-Optima blendstocks.

With the exception of the biodiesel surrogate molecules MeStearate and MeOleate, little measured biodegradability data exist for the Co-Optima blendstocks. MeStearate and MeOleate have actual testing data available as part of their complete Part 79 fuel registration showing biodegradability, aligning with the estimates presented here. The EPISuite estimates found only farnesane and 5-Et-4-Propylnonane were not biodegradable.

The diesel surrogate molecules, which are generally part of typical petroleum derived fuels, have some biodegradability data available, though it is limited. EPISuite estimated limited anaerobic biodegradability for cetane and BuCyclohexane (positive values in Table 4), but no other diesel surrogate molecules (negative values in Table 4) and aerobic biodegradability for Bucyclohexane and cetane.

Human and ecological health indicators are highly similar for the Co-Optima blendstocks and diesel surrogate molecules. The Co-Optima blendstocks were found to have lower chronic toxicity than the diesel surrogates and less potential to bioaccumulate.

5. Conclusions

Several promising Co-Optima blendstocks have previously been identified for use in MCCI engines. These blendstocks were: 2-nonanol, undecane, farnesane, 5-Et-4-PrNonane, HeHexanoate, MeDecanoate, 4-BH, dipentylether, 2-MeC15, 2Me-C17, MeStearate, and MeOleate. This analysis builds on that early analysis by providing additional detail on environmental metrics, including toxicity and biodegradability. This work is meant to provide additional information for decision makers for further evaluation of the potential for these molecules.

The Co-Optima bioblendstocks were compared to several diesel surrogate compounds to provide a more robust analysis. There is little literature information on many of these novel

bioblendstock molecules and QSARs were used to generate estimates to feed into the environmental models. Literature data existed for a few molecules, but in order to have an apples-to-apples comparison, estimates were used for all molecules. A comparison of estimated to measured values and their impact on model output will be the focus of future work.

The analysis found few differences between the Co-Optima blendstocks and the diesel surrogate molecules. Compartment partitioning analysis revealed all molecules partitioning between the air and soil compartment, with limited water solubility. The only exception was the 2-nonanol with nearly 30% predicted to partition into the water compartment.

The 2-nonanol had the highest water solubility compared to any other chemical in this analysis. The relative water solubility, while higher than any of the other diesel-like counterparts, was still orders of magnitude below many of the gasoline-range compounds evaluated in our previous work (Alleman and Smith 2019). All the compounds analyzed had little to no mobility, meaning migration between compartments was predicted to be very low. A range of soil-to-water coefficients was found; however, the magnitude of these values supports the estimates of relative mobility. The compounds would not be likely to migrate between compartments in the event of an accidental environmental release.

Predicted biodegradability for the potential Co-Optima blendstocks was generally improved over the diesel surrogates. Not all the blendstocks molecules were biodegradable, but typically they were no worse than the diesel surrogates. The improvement in biodegradability for some bioblendstocks may be an asset for these compounds going forward.

Generally, the blendstocks and diesel surrogates were predicted to show slight to non-toxic effects for acute human toxicity. Indicators of developmental toxicity varied, with some blendstocks and surrogate exhibiting predicted toxicity (2-nonanol; undecane; MeDecanoate; dibutyoxymethane; dipentylether; BuCyclohexane; cetane; and dodecylbenzene). The remaining molecules were categorized as non-toxicants (farnesane; 5-Et-4-PrNonane; 4-BH; 2MeC15; 2MeC17; MeStearate; MeOleate; a-MeNaph; transdecalin; isocetane; and tetralin).

Similar to the other metrics, the ecological exposure results are similar for the compounds studied. All of the compounds, whether Co-Optima blendstocks or diesel surrogates, exhibited high predicted toxicity to *D. magna*, though the blendstocks were less likely to bioaccumulate than the diesel surrogates. Some benefit was observed for the oxygenated blendstocks compared to the non-oxygenated ones.

Based on the models used in this analysis, there is little overall difference between the MCCI blendstocks and the diesel surrogate molecules. These results do not reveal significant showstoppers that would suggest caution in further evaluation of these molecules.

6. References

- “Protection of the Environment.” Code of Federal Regulations, Title 40 (2017): <https://ecfr.io/Title-40/pt40.18.79>.
- Alleman, Teresa L., and Dennis Smith. 2019. *Toxicology and Biodegradability of Tier Three Gasoline Blendstocks. Literature Review of Available Data*. Technical Report No. TP-5400-73239. Golden, Colorado: National Renewable Energy Laboratory.
- Anderson, J.E., D.M. DiCicco, J.M. Ginder, U. Kramer, T.G. Leone, H.E. Raney-Pablo, and T.J. Wallington. 2012. “High Octane Number Ethanol-Gasoline Blends: Quantifying the Potential Benefits in the United States.” *Fuel* 97:585–594.
- Bevan, C., T.L. Neeper-Bradley, R.W. Tyl, L.C. Fischer, R.D. Panson, J.J. Kneiss, and L.S. Andrews. 1997a. “Two-Generation Reproductive Study of Methyl tertiary-Butyl Ether (MTBE) in Rats.” *J. Appl. Toxicol.* 17 (S1):S13–S19.
- Bevan, C., R.W. Tyl, T.L. Neeper-Bradley, L.C. Fischer, R.D. Panson, J.F. Douglas, and L.S. Andrews. 1997b. “Developmental Toxicity Evaluation of Methyl tertiary-Butyl Ether (MTBE) by Inhalation in Mice and Rabbits.” *J. Appl. Toxicol.* 17 (S1): S21–S29.
- Bird, M.G., H.D. Burleigh-Flayer, J.S. Chun, J.D. Douglas, J.J. Kneiss, and L.S. Andrews. 1997. “Oncogenicity Studies of Inhaled Methyl tertiary-Butyl Ether (MTBE) in CD-1 Mice and F-344 Rats.” *J. Appl. Toxicol.* 17 (S1): S45–S55.
- Cardamone, L., M. Gocieva, M. Mancusi, R. Padovani, and L. Tamellini. (undated). *Chemistry, Toxicology, and QSAR: An Introduction*. <http://vega.marionegri.it/wordpress/wp-content/uploads/2011/09/antaresBook.pdf>.
- Cherkasov, A., E.N. Muratov, D. Fourches, A. Varnek, I.I. Baskin, M. Cronin, P. Gramatica, Y.C. Martin, R. Todeschini, V. Consonni, V.E. Kuz'min, R. Cramer, R. Benigni, C. Yang, J. Rathman, L. Terfloth, J. Gasteiger, A. Richard, and A. Tropsha. 2014. “QSAR Modeling: Where Have You Been? Where Are You Going To?” *J. Med. Chem.* 57(12):4977–5010. doi:10.1021/jm4004285.
- Chilcott, Robert P. (undated). “Compendium of Chemical Hazards: Diesel.” www.hpa.org.uk.
- Chow, E., J. Heywood, and R. Speth. 2014. “Benefits of a Higher Octane Standard Gasoline for the U.S. Light-Duty Vehicle Fleet.” SAE Technical Paper 2014-01-1961. doi:10.4271/2014-01-1961.
- Daughtrey, W.C., M.W. Gill, L.M. Pritts, J.F. Douglas, J.J. Kneiss, and L.S. Andrews. 1997. “Neurotoxicological Evaluation of Methyl tertiary-Butyl Ether in Rats.” *J. Appl. Toxicol.* 17 (S1):S57–S64.

- Department of Ecology, State of Washington. 2019. “Focus on: Environmental Harm from Oil Spills.” Publication 10-08-001.
<https://fortress.wa.gov/ecy/publications/documents/1008001.pdf>.
- Farrell, John, J. Holladay, and R. Wagner. 2018a. *Fuel Blendstocks with the Potential to Optimize Future Gasoline Engine Performance: Identification of Five Chemical Families for Detailed Evaluation*. Technical Report. U.S. Department of Energy, Washington, DC. DOE/GO-102018-4970.
- Farrell, John, R. Wagner, D. Gasper, and C. Moen. 2018b. “FY18 Year in Review.” U.S. Department of Energy, Washington, DC. DOE/GO-102019-5150.
- Fioroni, G., L. Fouts, J. Luecke, D. Vardon, N. Huq, E. Christensen, X. Huo, T. Alleman, R. McCormick, M. Kass, E. Polikarpov, G. Kukkapu, and R.A. Whitesides. 2019. “Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Mixing Controlled Compression Ignition Combustion.” SAE Technical Paper 2019-01-0570, doi:10.4271/2019-01-0570.
- “FY18 Year In Review.” https://www.energy.gov/sites/prod/files/2019/06/f64/Co-Optima_YIR2018_FINAL_LOWRES%20190619_0.pdf
- Graham, L.A. S.L. Belisle, and C.-L. Baas. 2008. “Emissions from Light-Duty Gasoline Vehicles Operating on Low Blend Ethanol Gasoline and E85.” *Atmos. Environ.* 42: 4498-4516.
- Huq, N.A., Huo, X., Hafenstine, F.R. Tifft, S.M., Stunkel, J., Christensen, E.D., Fioroni, G.M., Fouts, L., McCormick, R.L., Cherry, P.A., McEnally, C.S., Pfefferle, L.D., Wiatrowski, M.R., Benavides, P.T., Bidy, M.J., Connatser, R.M., Kass, M.D., Alleman, T.J., St. John, P., Kim, S., Vardon, D.R. 2019. “Performance-Advantaged Ether Diesel Bioblendstock by *a priori* Design” *Proc Nat Acad Sci* doi.org/10.1073/pnas.1911107116.
- Karavalakis, G., T.D. Durbin, M. Shrivastava, Z. Zheng, M. Villela, and H. Jung. 2012. “Impacts of Ethanol Fuel Level On Emissions of Regulated and Unregulated Pollutants from a Fleet of Gasoline Light-Duty Vehicles.” *Fuel* 93: 549–558.
- Leone, T.G., E.D. Olin, J.E. Anderson, H.H. Jung, and M.H. Shelby. 2014. “Effects of Fuel Octane Rating and Ethanol Content on Knock, Fuel Economy, and CO₂ for a Turbocharged DI Engine.” *SAE Int. J. Fuels Lubr.* 7(1): 9–28. doi:10.4271/2014-01-1228.
- Leone, T.G., J.E. Anderson, R.S. Davis, A. Iqbal, R.A., Reese II, M.H. Shelby, and W.M. Studzinski. 2015. “The Effect of Compression Ratio, Fuel Octane Rating, and Ethanol Content on Spark-Ignition Engine Efficiency.” *Environ. Sci. Technol.* 49, pp 10778–10789.

- Lington, A.W., D.E. Dodd, S.A. Ridlon, J.F. Douglas, J.J. Kneiss, and L.S. Andrew. 1997. "Evaluation of 13-Week Inhalation Toxicity Study on Methyl t-Butyl Ether (MTBE) in Fischer 344 Rats." *J. Appl. Toxicol.* 17 (S1):S37–S44.
- McCormick, R.L., G. Fioroni, L. Fouts, E. Christensen, J. Yanowitz, E. Polikarpov, K. Albrecht, D.J. Gaspar, J. Gladden, and A. George. 2017. "Selection Criteria and Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Advanced Spark-Ignition Engines." *SAE Int. J. Fuels Lubr.* 10(2):2017, doi:10.4271/2017-01-0868.
- McKee, R.H., Z.A. Wong, S. Schmitt, P. Beatty, M. Swanson, C.A. Schreiner, and J.L. Schardein. 1990. "The Reproductive and Developmental Toxicology of High Flash Aromatic Naphtha." *Toxicol. Ind. Health* 6 (3–4):441–460.
- Miller, M.J., E.S. Ferdinandi, M. Klan, L.S. Andrews, J.F. Douglas, and J.J. Kneiss. 1997. "Pharmacokinetics and Disposition of Methyl t-Butyl Ether in Fischer-344 Rats." *J. Appl. Toxicol.* 17 (S1): S3–S12.
- National Renewable Energy Laboratory. 2020. "Co-Optimization of Fuels & Engines: Fuel Properties Database." Accessed August 11, 2020. <https://www.nrel.gov/transportation/fuels-properties-database/>.
- Risher, J.F, and S.W. Rhodes. (1995). "Toxicological Health Profile for Fuel Oils." U.S. Department of Health and Human Services. <https://www.atsdr.cdc.gov/toxprofiles/tp75.pdf>.
- Schultz, T.W., M.T.D. Cronin, and T.I. Netzeva. 2002. "The Present Status of QSAR in Toxicology." *Journal of Molecular Structure: THEOCHEM* 622(1-2):23–28. [https://doi.10.1016/S0166-1290\(02\)00615-2](https://doi.10.1016/S0166-1290(02)00615-2).
- Seagrave, J., J.D. McDonald, A.P. Gigliotti, K.J. Nikula, S.K. Seilkp, M. Gurevich, and J.L. Mauderly. 2002. "Mutagenicity and *in Vivo* Toxicity of Combined Particulate and Semivolatile Organic Fractions of Gasoline and Diesel Engine Emissions." *Toxicological Sciences* 70: 212–226.
- Stein, R., J. Anderson, and T. Wallington. 2013. "An Overview of the Effects of Ethanol-Gasoline Blends on SI Engine Performance, Fuel Efficiency, and Emissions." *SAE Int. J. Engines* 6(1):470-487. doi:10.4271/2013-01-1635.
- Trent University. 2004. "Level I, Fugacity-Based Environmental Equilibrium Partitioning Model." Canadian Environmental Modeling Centre, Trent University, Peterborough, Ontario, Canada.
- Tyson, K. Shaine. 1998. *Biodiesel Research Progress 1992-1997*. NREL/SR-580-24433. Golden, Colorado: National Renewable Energy Laboratory. <https://www.nrel.gov/docs/legosti/fy98/24433.pdf>

- U.S. Environmental Protection Agency. 2007. “Guidance for Biodiesel Producers and Biodiesel Blenders/Users.” <https://19january2017snapshot.epa.gov/sites/production/files/2015-08/documents/420b07019.pdf>.
- von Stackelberg, K., J. Buonocore, P.V. Bhave, and J.A. Schwartz. 2013. “Public Health Impacts of Secondary Particulate Formation from Aromatic Hydrocarbons in Gasoline.” *Environmental Health* 12:19.
<https://ehjournal.biomedcentral.com/track/pdf/10.1186/1476-069X-12-19>
- Zielinska, B., J. Sagebiel, J.D. McDonald, K. Whitney, and D.R. Lawson. 2012. “Emission Rates and Comparative Chemical Composition from Selected In-Use Diesel and Gasoline-Fueled Vehicles.” *Journal of the Air & Waste Management Association* 54(9): 1138–1150. doi: 10.1080/10473289.2004.10470973.

Appendix

Figure A-1. Illustrative compartment partitioning for 2-nonanol.

Figure A-2. Illustrative compartment partitioning for undecane.

Figure A-3. Illustrative compartment partitioning for farnesane.

Figure A-4. Illustrative compartment partitioning for 5-Et-4-PrNonane.

Figure A-5. Illustrative compartment partitioning for HeHexanoate.

Figure A-6. Illustrative compartment partitioning for MeDecanoate.

Figure A-7. Illustrative compartment partitioning for Dibutoxymethane.

Figure A-8. Illustrative compartment partitioning for 4-BH.

Figure A-9. Illustrative compartment partitioning for Dipentylether.

Figure A-10. Illustrative compartment partitioning for 2-MePentadecane.

Figure A-11. Illustrative compartment partitioning for 2-MeHeptadecane.

Figure A-12. Illustrative compartment partitioning for MeStearate.

Figure A-13. Illustrative compartment partitioning for MeOleate.

Figure A-14. Illustrative compartment partitioning for α -MeNaph.

Figure A-15. Illustrative compartment partitioning for transdecalin.

Figure A-16. Illustrative compartment partitioning for isocetane.

Figure A-17. Illustrative compartment partitioning for BuCyclohexane.

Figure A-18. Illustrative compartment partitioning for cetane.

Figure A-19. Illustrative compartment partitioning for tetralin.

Figure A-20. Illustrative compartment partitioning for dodecylbenzene.

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