

The Feasibility of Using Raw Liquids from Fast Pyrolysis of Woody Biomass as Fuels for Compression-Ignition Engines: A Literature Review

Charles J. Mueller
Sandia National Laboratories

ABSTRACT

This study summarizes the peer-reviewed literature regarding the use of raw pyrolysis liquids (PLs) created from woody biomass as fuels for compression-ignition (CI) engines. First, a brief overview is presented of fast pyrolysis and the potential advantages of PLs as fuels for CI engines. Second, a discussion of the general composition and properties of PLs relative to conventional, petroleum-derived diesel fuels is provided, with emphasis on the differences that are most likely to affect PL performance in CI-engine applications. Next, a synopsis is given of the peer-reviewed literature describing experimental studies of CI engines operated using neat PLs and PLs combined in various ways with other fuels. This literature conclusively indicates that raw PLs and PL blends cannot be used as “drop-in replacements” for diesel fuel in CI engines, which is reflected in part by none of the cited studies reporting successful operation on PL fuels for more than twelve consecutive hours. Based on the reported failure modes, some recommendations are offered for improving performance, reliability, and safety when fueling CI engines with PLs. It appears that PL-derived fuels are most likely to find sustainable CI-engine applications only after a cost-effective pre-use processing strategy is identified to address significant issues regarding fuel instability, materials incompatibilities (e.g., corrosivity), poor ignition quality, high viscosity, and undesirable water/solids/energy contents.

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1. INTRODUCTION

Pyrolysis is defined as the “chemical decomposition of organic materials by heating in the absence of oxygen” [1]. Fast pyrolysis is typically chosen for liquid-fuel production because it gives the highest liquid yields from woody biomass [2], where rapid heating and short residence time of the pyrolysis products in the vapor phase are critical for maximizing the liquid yield [3]. Liquid yields may be as high as 70-80% of the starting dry weight of the biomass [4]. The fast pyrolysis processes considered in this study involve heating a woody-biomass feedstock to ~500 °C in 0.5 - 2 s in an inert environment, followed by rapid cooling to produce pyrolysis liquids, non-condensing gases, char, and ash [5,6].

In this study, the liquid fraction of the pyrolysis products will be called pyrolysis liquid (PL). PL is also known as pyrolysis oil, py oil, bio-oil, bio-crude oil, wood liquid, liquid smoke, wood distillate, pyroligneous acid, and liquid wood [5].

A number of excellent review articles on various aspects of PLs exist. A succinct overview of the production,

characterization, and particularly the applications of PLs is presented in [4]. (The review in [7] is similar to that in [4].) PL production, chemistry, and feedstock effects are thoroughly reviewed in [5], and CI engine applications are reviewed in [8].

The use of fast pyrolysis of biomass has been considered as a means to produce fuels for compression-ignition (CI) engines since its conception in 1976 [9], and the first known peer-reviewed study of PL fueling of a CI engine was published in 1993 [10]. PLs have a number of potential advantages over conventional petroleum-derived fuels for CI engines, particularly when the PLs are produced from waste biomass and used in stationary diesel generators to produce electrical power. These advantages include:

1. Potentially low (even negative) feedstock cost [11]
2. Low net CO₂ production [5]
3. Inherently low sulfur content for compatibility with advanced aftertreatment systems [5]

4. Potentially lower NO_x emissions than diesel-fueled operation [12]
5. Enhanced energy security by use of locally available biomass feedstocks [5]
6. Well-suited for use in remote, off-power-grid locations [12]
7. Easier to handle than solid biomass or syngas from gasification of biomass [13]
8. Desirable storability, transportability, and high energy density characteristics similar to those of conventional hydrocarbon fuels [8]

Despite the above advantages, “no real fuel markets have yet been established for this biofuel” [6]. The purpose of this study is to survey the peer-reviewed literature on PLs to provide an improved understanding of the reasons underlying this fact, and to identify approaches for overcoming barriers to the broader use of this important renewable fuel in CI engines.

1.1. Pyrolysis Feedstock and Product Compositions

Fast pyrolysis can be used to convert many different types of organic materials (*e.g.*, forest and agricultural residues, used tires, municipal solid waste) into PLs. [Figure 1](#) shows the composition of pine biomass before pyrolysis. The majority of the biomass is comprised of cellulose and hemicellulose, which are polysaccharides, *i.e.*, polymers of simple sugars. Next most abundant is lignin, which is an amorphous, crosslinked polymer comprised of “an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units.” The inorganics may include potassium, calcium, magnesium, phosphorus, and sodium compounds. The organic extractives are species that can be removed from the biomass by solvent extraction or steam distillation, and they include fats, waxes, alkaloids, proteins, phenolics, simple sugars, and other compounds (see [5] and Ch. 6 of [14]).

[Figure 2](#) shows a typical product distribution for the pyrolysis of woody biomass. Pyrolysis causes a fraction of the biomass polymers to break apart, producing compounds that resemble their building blocks, *e.g.*, cellulose produces levoglucosan and lignin produces phenolics as well as phenolic oligomers [5] with molecular weights ranging from 900 to 2500 [4]. Some of the oxygen and hydrogen in the biomass combine to form water, which is added to the moisture content of the original biomass in the PL. Non-condensing gases also are formed via cracking and water-gas shift reactions. The inorganics tend to form solid ash (*i.e.*, alkali-metal carbonates and/or oxides [15]), and some fraction of the organic composition (particularly lignin) forms solid char [5]. Char is defined as “fine carbonaceous powder that is separated from the vapors of biomass during pyrolysis” [1].

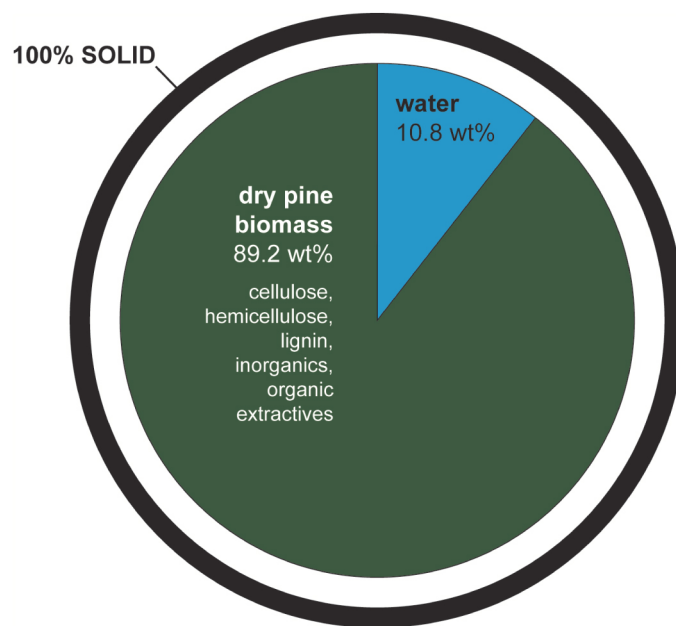


Figure 1. Feedstock composition for pine biomass, from [6]. Active drying is required to achieve the low water content shown. The water is present as moisture distributed throughout the biomass chemical structure [5].

From an elemental standpoint, PLs typically contain 35-40 wt% oxygen, as well as 54-58 wt% carbon, 5.5-7.0 wt% hydrogen, and 0-0.2 wt% nitrogen [4]. This elemental distribution much more closely resembles that of the biomass from which it was derived (for wood: 52 wt% carbon, 6.0 wt% hydrogen, and 42 wt% oxygen) [5] than that of a typical hydrocarbon diesel fuel (87.0 wt% carbon and 13.0 wt% hydrogen) [16]. The high oxygen content of PLs leads to a stoichiometric air/fuel mass ratio of ~7, which is approximately half the stoichiometric air/fuel ratio of conventional hydrocarbon diesel fuels [4].

PLs typically contain several hundred distinct organic compounds, nearly all of which are oxygenated. Molecular structures of some representative PL oxygenates are shown in [Fig. 2](#). The composition of the pyrolysis product mixture is difficult (if not impossible) to quantitatively determine at present [5], though substantial progress is being made in this regard (see, *e.g.*, [17,18,19,20]). The product-mixture composition is dependent on the biomass feedstock composition and the pyrolysis reaction parameters, including biomass preconditioning (particle size and moisture content), heating rate, pyrolysis temperature, vapor-phase residence time, cooling rate, and liquid recovery system [4,5].

The composition of PLs (particularly the water content and high degree of oxygenation) is dramatically different from the composition of conventional petroleum-derived diesel fuels. [Figure 3](#) shows the composition of a typical petroleum-derived US #2 ultra-low-sulfur diesel fuel by hydrocarbon class. Such fuels are effectively comprised

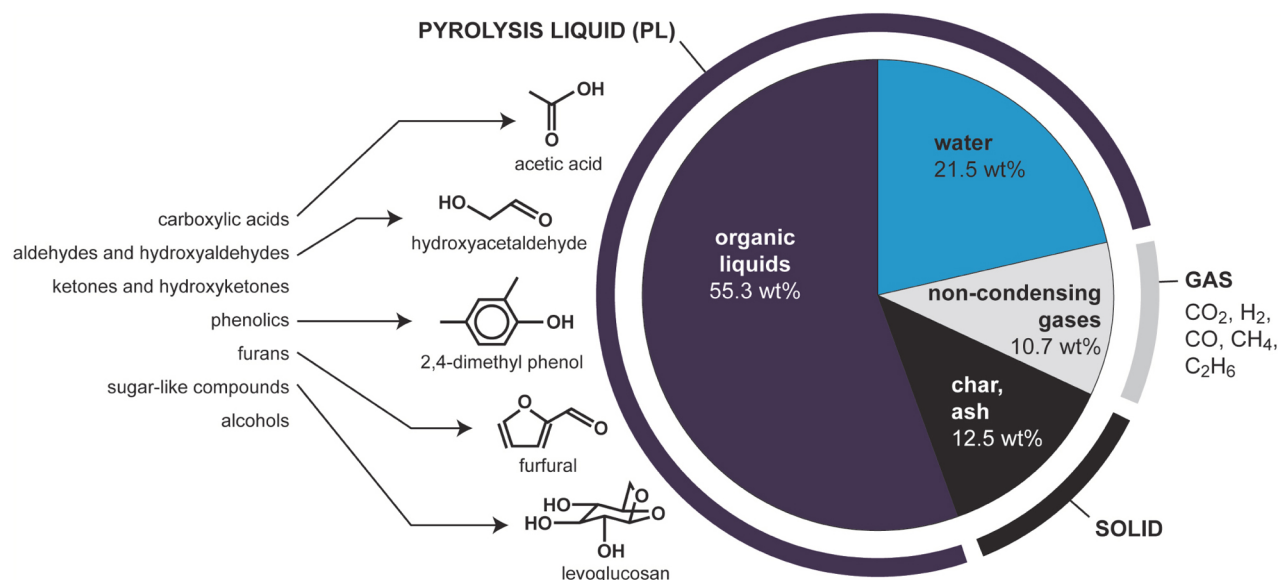


Figure 2. Typical product distribution for the pyrolysis of pine biomass, from [6] and [4]. Water content has increased relative to the biomass feedstock (cf. Fig. 1), and the biomass has been transformed from solid into gaseous, liquid, and solid fractions. Molecular structures of representative compounds within selected PL oxygenate classes are provided for reference.

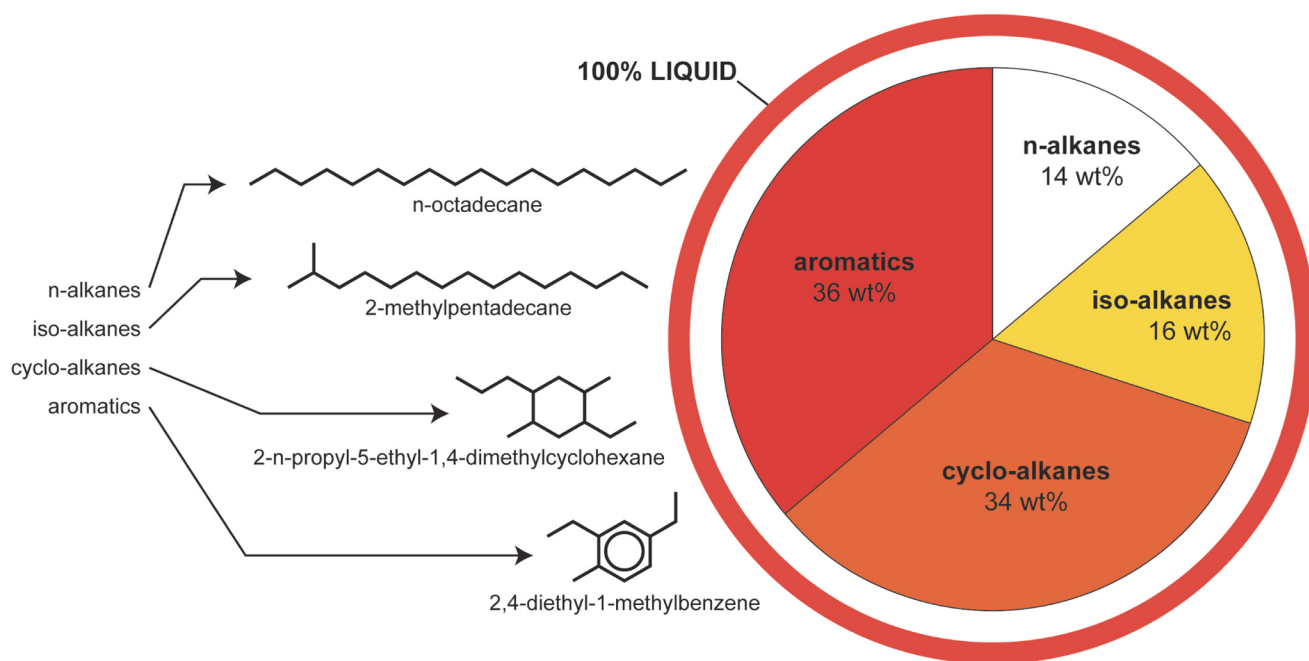


Figure 3. Typical #2 ultra-low-sulfur diesel fuel composition, from [16]. The molecular structure of a representative compound within each hydrocarbon class is provided for reference.

entirely of hydrocarbons, typically containing < 1 wt% oxygen (see Table 1 in [16]).

1.2. Properties of PLs

The compositional characteristics of PLs discussed above determine to a large extent the performance characteristics of PLs as fuels for CI engines. This section provides a brief

overview of PL properties with a focus on engine applications.

1.2.1. Water content

The most abundant single compound in a typical PL is water, at 15-30 wt%. PLs are typically microemulsions with an aqueous solution of carboxylic acids, aldehydes, ketones, and sugar-like compounds as the continuous phase and

mainly lignin-derived water insolubles as the distributed phase [5,6]. The high water content and polar nature of most PL compounds lead to PLs being insoluble in conventional hydrocarbon diesel fuels but soluble in ethanol [10]. The upper limit for water and sediment for all grades of diesel fuel in the ASTM D975-11b specification [21] is 0.05 vol% by ASTM D2709 [22]. Clearly, PLs do not satisfy this requirement. Water cannot be removed easily from PLs [5]. Indeed it is not usually desired to remove the water because the organics in PLs include both hydrophilic and hydrophobic compounds, with the hydrophilic species dissolved in the aqueous fraction [4]; hence, removal of the water would cause many of the hydrophilic species to come out of solution.

1.2.2. Corrosivity

The presence of ~5 wt% carboxylic acids (mostly acetic and formic) in the aqueous phase [6] contributes to the low pH (~2.6 for PL from pine [7]) and hence the corrosivity of PLs. The corrosivity of PLs tends to increase with temperature and water content. PLs are corrosive to carbon steels, aluminum [4], and Viton [12], but compatible with polytetra-fluoroethylene (PTFE), at least some stainless steels, and ethylene propylene diene monomer (EPDM) rubber [12]. The corrosion limit for all grades of diesel fuel in the ASTM D975-11b specification [21] is No. 3 by ASTM D130 [23]. Based on the results in Table 8 of [24] and engine testing results discussed below, it is unlikely that unmodified PLs will satisfy this requirement.

1.2.3. Viscosity

The viscosity of PLs can vary from 35 - 1000 mm²/s @ 40 °C depending on feedstock and process conditions. Higher water content correlates with lower PL viscosity [4]. Adding methanol, acetone [4], or ethanol [7] to a PL also can lower its viscosity. The viscosity of a PL generally increases with time due to liquid-phase polymerization and oxidation reactions [4,10]. The maximum kinematic viscosity for all grades of #2 diesel fuel in the ASTM D975-11b specification [21] is 4.1 mm²/s at 40 °C by ASTM D445 [25]. Moderate preheating is effective at lowering the viscosity of PLs because viscosity decreases more rapidly with temperature for PLs than it does for conventional petroleum oils [10]. Even with preheating to 50 °C, PL viscosities are typically in the range of 40- 100 mm²/s [4], which is well outside of the specification.

1.2.4. Stability

The two primary modes of instability of PLs are hydrophilic/hydrophobic phase separation of the PL microemulsion and liquid-phase chemical reactions. Active mixing within storage tanks may prevent phase separation [1], but preventing chemical reactions is more challenging. PLs are not created in thermodynamic equilibrium, and as a result, reactions during storage tend to move the composition of PLs toward thermodynamic equilibrium. Such reactions

can lead to an increase in viscosity as discussed in the preceding paragraph. While increasing the PL temperature can temporarily compensate for the viscosity increase, it also accelerates the rate of liquid-phase reactions [1]. The organic acids in PLs tend to be reactive with other fuel compounds [7] and materials in contact with the fuel [4]. The char contains metals (especially potassium) that can catalyze reactions in the liquid phase, so removing the char particles can enhance the stability of a PL [26]. During storage, the carbonyl content tends to decrease, while the water-insoluble fraction tends to increase [6]. The polymerization reactions can produce solids that can lead to improper operation of fuel-injection equipment (e.g., [27]).

1.2.5. Solids

PLs are typically dark brown to black in color (see Fig. 4), and the dark color comes from < 10-μm-diameter char particles suspended in the liquid. When researchers at the National Renewable Energy Laboratory (NREL) hot-filtered their pyrolyzer products while still in the vapor phase to remove these fine char particles, the resultant PL was amber in color [26]. PLs must be filtered to remove solid char and ash particles before use in a CI engine [12]. NREL researchers showed that hot-gas filtering can yield < 2 ppm alkali metals and < 2 ppm alkaline-earth metals in PLs [7], which would lead to very low ash levels. Nevertheless, as discussed above, polymerization of organic species in the liquid phase can lead to the formation of solid particles in the fuel after filtration [27]. The ash and solids contents of PLs are typically 0-0.2 wt% and 0.2-1 wt%, respectively [4], whereas the maximum ash content (by ASTM D482 [29]) of #2 diesel fuels is 0.01 wt% [21]. Hence, it is expected that PL solids could cause problems during engine operation, which is consistent with the results of the experimental engine studies discussed below.



Figure 4. PL pouring into a beaker. PLs are typically dark brown to black in color [28], with a viscosity higher than that of conventional diesel fuel [4,21], and characterized by a smoky odor [26].