Fuel 215 (2018) 123–141

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Review article

Fungal metabolites as precursors to renewable transportation fuels

Mark G. Butcher, Pimphan A. Meyer, Richard T. Hallen, Karl O. Albrecht, Christopher K. Clayton, Evgueni Polikarpov, Kenneth G. Rappe, Susanne B. Jones, Jon K. Magnuson*

Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, Richland, WA 99352, USA

A R T I C L E I N F O

Keywords:
Biofuel
Biomass
Biosynthesis
Blendstock
Hydroprocessing
Polyketide
Terpene
Terpenoid

A B S T R A C T

Fungi are known to produce hundreds of different polyketide, terpene, and terpenoid compounds and based on their chemical structures, 33 of these were selected for further assessment to identify compounds with potential for liquid transportation fuels. Eight of the 33 compounds were identified as having potential as gasoline blend components. Based on predicted boiling points and octane numbers, 2-ethyl-5,5-dimethyl-1,3-cyclopentadiene, sabinene, isobutyric acid,1,8-cineole and linalool met the boiling point and octane number requirements used for the assessment, while 2-ethyl-5,5-dimethyl-1,3-cyclopentadiene and isobutyric acid would require some upgrading. Limonene, isoamyl acetate, and 2,2,5,5-tetramethyl-3-hexanone also have gasoline blend potential without upgrading. For diesel fuel, only 3,3,5-trimethyldecane met the boiling point, cetane number, and flashpoint requirements used for the assessment; however, with upgrading, 18 of the 33 compounds evaluated could potentially serve as blend components of diesel fuel. None of the 33 compounds without upgrading met the four ASTM D1655 specifications for Jet A and Jet A-1 fuel, but 3,3,5-trimethyldecane and limonene were very close. With chemical upgrading, 22 of the 33 compounds could have potential as jet fuel blend components. The monoterpene limonene and six sesquiterpenes were identified as fungal-derived compounds that with upgrading potentially could serve as components of high-energy jet, missile, or diesel fuels.

The increasing availability of fungal genomes and transcriptomes enables the identification of important metabolic pathways for hydrocarbon production. The number of fungal-based compounds having potential for use in hydrocarbon fuels and products is increasing as new compound and pathway discoveries are made and advances in metabolic engineering and synthetic biology enable the production of these compounds. Several challenges remain including increasing carbon flux toward hydrocarbon fuel precursors in primary metabolism, increasing the low titers of hydrocarbons produced, and establishing robust host strains. Also, more fuel property testing of fungal-derived compounds individually or in fuel blendstocks is needed to determine the true potential of these compounds in liquid transportation fuels.

1. Introduction

The demand for liquid transportation fuels is expected to increase as the world's population continues to grow and greater global industrialization is realized [1,2]. In a 2010 report, the National Research Council stated, "There seems to be little doubt that … internal combustion engines will be the dominant prime mover for light-duty vehicles for many years, probably decades. … it is important to maintain an active ICE (internal combustion engine) and liquid fuels R&D program at all levels.…" [3]. The development and use of sustainable liquid transportation fuels produced from renewable resources has attracted attention for addressing concerns about the environment [1,2,4–8]. Various fungi are recognized as being excellent platforms for taking advantage of biosynthetic routes to producing hydrocarbon fuels and their precursors [9]. Fungal organisms synthesize energy-dense isoprenoid and polyketide hydrocarbons through known metabolic pathways with potential to be engineered for production of infrastructure-compatible biofuel precursors from lignocellulosic biomass. A considerable number of these compounds have properties that are similar to conventional petroleum-based fuels [4]. Although there are

Abbreviations: ACD, Advanced Chemistry Development; ASTM, American Society for Testing and Materials; CN, cetane number; CO, carbon monoxide; CoA, acetyl-coenzyme A; CRC, Coordinating Research Council, Inc; DCN, derived cetane number; ICE, internal combustion engine; Ir, iridium; JP, jet propellant; MON, motor octane number; NHOC, net heat of combustion; NO_x, nitrogen oxides; Pt, platinum; RON, research octane number; SBIR, Small Business Innovation Research Program

* Corresponding author.

E-mail addresses: mark.butcher@pnnl.gov (M.G. Butcher), Pimphan.Meyer@pnnl.gov (P.A. Meyer), richard.hallen@pnnl.gov (R.T. Hallen), Karl.Albrecht@pnnl.gov (K.O. Albrecht), christopher.clayton@pnnl.gov (C.K. Clayton), Evgueni.Polikarpov@pnnl.gov (E. Polikarpov), ken.rappe@pnnl.gov (K.G. Rappe), Sue.Jones@pnnl.gov (S.B. Jones), Jon.Magnuson@pnnl.gov (J.K. Magnuson).

https://doi.org/10.1016/j.fuel.2017.10.052
Received 26 July 2017; Received in revised form 6 October 2017; Accepted 10 October 2017
0016-2361/

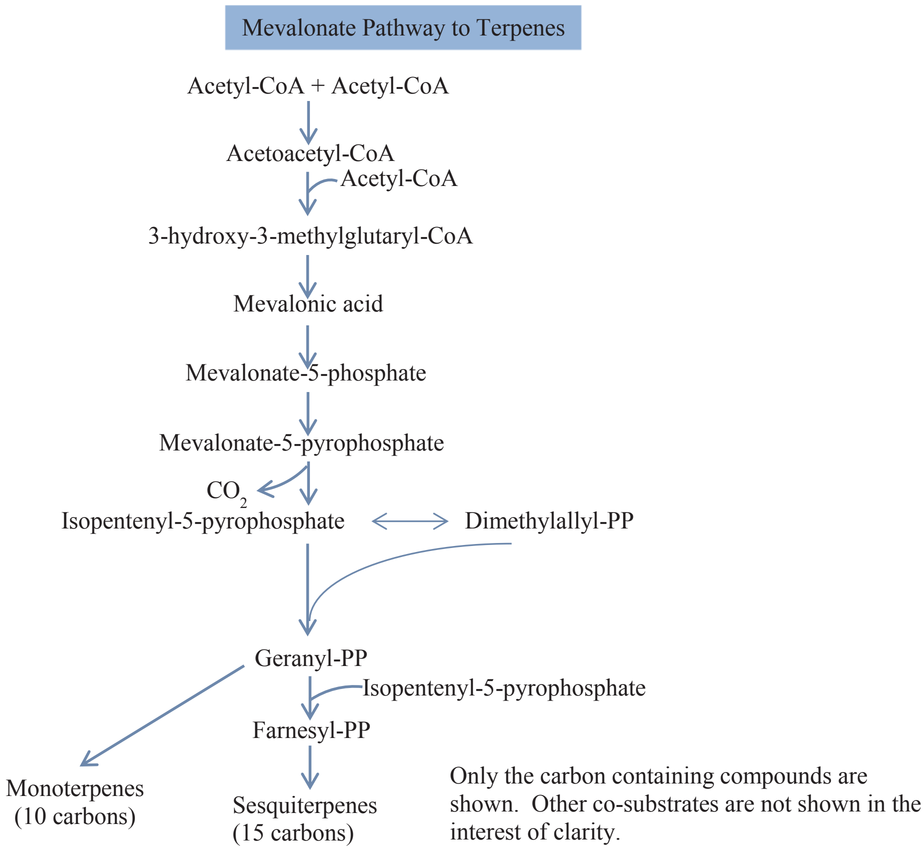

Fig. 1. Mevalonate pathway to monoterpenes and sesquiterpenes.

many secondary metabolites, they are naturally produced at low levels by the organisms that do not appear to need them under normal development and growth conditions [10]. As more and more of these compounds are discovered and candidates are selected for commercial applications, the overarching challenge is to increase titer, rate, and yield to economically sustainable levels so their benefits can be realized [11,12]. This requires development of, or improvements to, 1) metabolic pathways and other aspects of the biocatalysts (fungi) and 2) bioprocesses to facilitate production of the desired compounds at the required levels [4,12]. Advances in metabolic engineering are making the generation of applicable host microbes that produce biofuels with properties similar to petroleum-based fuels a reality with considerable potential [7].

For this study, first the literature was searched for isoprenoid and polyketide compounds produced or predicted to be produced by filamentous fungi or yeasts. Second, Pacific Northwest National Laboratory (PNNL) fuel chemists evaluated the chemical structures of approximately 600 terpenes and 250 polyketides found in the literature to identify compounds expected to have potential for liquid hydrocarbon fuels or fuel precursors. Third, based on the results of the initial evaluation, 33 compounds were selected for further assessment. Fourth, key fuel properties were used to assess the suitability of the 33 compounds for use in specific fuels such as gasoline, diesel, jet, or high-energy fuels. The primary purpose of this study was to evaluate non-lipid compounds produced by fungi that have a variety of chemical functional groups to provide examples of compounds having potential as fuel compounds, rather than an exhaustive list of every candidate compound.

2. Hydrocarbon metabolites derived from fungal biosynthesis

Fungi are known to produce a wide variety of secondary metabolites that can be further divided into several classes, namely, terpenes and terpenoids, polyketides, non-ribosomal peptides, and alkaloids [8,13]. Secondary metabolites from fungi encompass much of the diversity found in organic chemistry with regard to structure and functional groups. They can be relatively simple linear, branched or ring structures, analogous to paraffins, isoparaffins and cycloparaffins, respectively, or they can be very unique complex structures containing a combination of rings and branches. Terpenes, terpenoids, and polyketides were the primary focus of this study because many of them have few or no oxygen atoms and are suitable candidates for 1) use as liquid hydrocarbon transportation fuel or 2) upgrading to liquid hydrocarbon transportation fuel through known conversion pathways.

2.1. Terpenes and terpenoids

Terpenes are hydrocarbons that are essentially polymers of isoprene units (C_5H_8:). They can be linear or cyclic and saturated or unsaturated, with their biosynthesis often triggered by environmental cues such as carbon or nitrogen sources and concentrations, ambient temperature, light, and pH [13]. The terpenes in the liquid fuel range are the monoterpenes (C_{10}), sesquiterpenes (C_{15}) and diterpenes (C_{20}), which are composed of two, three and four units of isoprene, respectively [14].

Biosynthesis of terpenes is straightforward; they are formed by the action of a single specific terpene synthase (aka, terpene cyclase). Terpenoids are functionalized derivatives of terpenes that contain aldehyde, ketone, or hydroxyl groups. In addition to the terpene synthase, accessory enzymes are needed to add these functional groups to the hydrocarbon backbone of the parent terpene. Large numbers of terpenes and terpenoids have been isolated from fungi with the majority being sesquiterpenes and their derivatives [15]. In fungi, terpenes and terpenoids are biosynthesized from the C_5 precursors isopentenyl pyrophosphate and dimethylallyl pyrophosphate, which are derived from the intermediate mevalonic acid, which is in turn synthesized