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Catalytic cracking of sterol-rich yeast lipid

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HIGHLIGHTS

- Sterol rich lipid was converted to a fuel in a single catalytic cracking step.
- The cracking of sterol liberates hydrogen, resulting in a reduced olefin content.
- Cracking over Pd/C gave a fuel with high ratio of linear alkanes & ~10% aromatics.
- The resulting hydrocarbon fuel could be blended up to 50% with ULSD.

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ABSTRACT

Microbial lipids offer a promising feedstock for renewable biofuels. However, one of the major concerns with their conversion from lipids into suitable fuels is the high sterol content of the lipid. This is especially problematic for lipids obtained from oleaginous yeasts, as there are some indications that the sterol content could inhibit catalyst performance during hydrotreating. In this investigation a sterol-rich model feedstock (a 50:50 mixture of cholesterol and rapeseed oil, "RC50") and an unrefined microbial lipid derived from the oleaginous yeast *Metschkownia pulcherrima* were converted to a diesel-like fuel in a single step via catalytic cracking. Far from reducing catalyst performance the cracking of the sterol groups liberated hydrogen, resulting in a reduction in the olefin content as well as an increase in the aromatic content of the fuel. The cracking of RC50 over Pd/C resulted in a fuel with a comparable product distribution to ultra-low sulphur diesel (ULSD), with high levels of linear alkanes and approximately 10 wt% aromatics. Cracking of unrefined yeast lipid over Pd/C was shown to result in an energy dense, hydrocarbon fuel suitable for marine applications (unblended) or a road transport fuel at 50% v/v blends with ULSD.

1. Introduction

The mitigation of climate change by reducing global carbon emissions, whilst meeting an ever-increasing energy demand, is one of the biggest challenges of the 21st century. Emission reductions are particularly hard to achieve within the transportation sector, which accounts for 26% of total global energy consumption [1], mainly due to its heavy reliance on energy-dense liquid fuels. Biofuels are widely seen as an important contributor to help reduce short- to medium-term emissions until non-carbon based technologies can be widely introduced [2]. However, for biofuels to have a positive impact on global energy markets the key technological challenges that need to be addressed are associated with improving the quality of the fuel produced and ensuring the sustainability of its production.

One of the major sources of biofuels are glyceride lipids, which can be transesterified into biodiesel, comprised of fatty acid methyl esters. While biodiesel is fully miscible with diesel, fatty acid methyl esters have high cloud points, low energy densities and low oxidative stability, which have restricted their maximum blend levels to 7% (v/v) with ULSD in the EU [3,4]. Increasing the future use of bio-derived fuels therefore necessitates the development of higher-quality biofuels with more compatible properties to USLD. ULSD is a complex mixture of straight-chain and branched alkanes, cycloalkanes and aromatics. Generally, high levels of long chain alkanes in ULSD will result in higher cetane numbers and higher energy density, while the presence of branched components improves the low temperature behaviour. In addition, ULSD typically contains up to 20 wt% of aromatic compounds, which provide vital lubrication for the fuel injection system.

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In an attempt to improve the performance of bio-derived fuels, new processes for producing biofuels with similar hydrocarbon compositions to ULSD are being developed and tend to fall within one of two separate approaches [5]. The first approach uses hydrotreating, which involves the deoxygenation of triglycerides into linear chain alkanes, over Pd, Pt, Ni, Ru, Os, Rh or Ir catalysts supported on a range of zeolites, aluminosilicates or activated carbons [6,7]. This process is followed by additional isomerisation and cracking reactions over Pt or Pd catalysts on zeolite supports, which improve the low temperature properties of the resulting hydroprocessed ester and fatty acid ("HEFA") fuels [8]. A number of commercial hydrotreating processes for producing HEFA fuels have been licenced by companies such as Neste Oil (NExBTL), Syntroleum (Bio-Synfining™) and Honeywell UOP/Eni (Ecofining™) with the first renewable fuel plants having come into operation over the last few years [9–11]. However, as well as consuming significant amounts of hydrogen this method has the drawback of producing fuels with insufficient aromatic content; and must be blended with diesel prior to use to achieve the required lubrication and performance.

The second approach that is capable of converting lipids into suitable fuels with incorporated aromatic components (and the approach that is examined in this work) is catalytic cracking. Catalytic cracking has gained significant interest over the last thirty years after Mobil's development of the ZSM-5 zeolite catalyst. This catalyst was shown to convert a wide range of feedstocks (such as methanol, latex and corn oil) into a uniform product mix with high aromatic content and good selectivity towards a gasoline-type fuel in a single step [12,13]. Together with ZSM-5, Beta and Y zeolites are the most widely tested zeolites, but have been unable to match the high gasoline yields and low coking performance of the former [14–16]. More recently, attempts have been made to modify the catalyst structure by coating or mixing zeolite catalyst with mesoporous silica, and have helped to increase aromatics selectivities and reduce coke deposition on the catalysts [17,18]. As catalytic cracking is usually carried out at atmospheric pressures of inert gas (rather than requiring an external source of H_2, as is the case for hydrotreating) it could potentially result in a comparatively less expensive and more sustainable process for biofuel production. However, this also poses a major challenge, as the lack of hydrogen has been linked to extensive catalyst coking due to the formation of 'allyl-carbenium' ions from the glycerol backbone [19]. Side product formation of hydrocarbon gases, LPGs and solid char is another issue, resulting in low liquid yields of around 40–50% [14,20–23].

By far the greatest determinant of the sustainability of a biofuel is the sustainability of the feedstock [24], which has prompted research into alternative sources such as from oleaginous microbes. Many microalgae, fungal and yeast species are classed as oleaginous yet only phototrophic microalgae have been significantly investigated as a biofuel feedstock to date [25]. Microalgae show great potential as a fuel source because of high theoretical lipid yields, but harnessing the CO_2 needed for growth, expensive extraction steps and low growth rates are limiting commercial development. In contrast, oleaginous heterotrophic species, can grow in dense colonies and can produce yields of 100 g L^{-1} over a week in optimized aerobic conditions [26]. While traditionally yeasts are grown on sugars sourced from first generation crops, recent scientific breakthroughs have seen more diverse cellulosic sources (and potentially waste cellulosic materials) being utilised [27,28], with certain species producing lipids totalling over 60% of the dry weight under suitable conditions [29]. However, a major challenge in converting microbial lipids is in the complexity of the oils, which can include compounds such as phospholipids, carotenoids and most notably a wide variety of sterols including ergosterol, sitosterol and cholesterol [30]. While sterols are present to up to 5 wt% in algal lipids they can total up to 50 wt% in some yeast oils [31–34], which can pose problems for processing of these feedstocks via conventional transesterification or hydrotreating routes. For transesterification reactions, the high sterol content would reduce the yield and potentially saponify the catalyst, further increasing the cost of the process. In the hydrotreatment of lipids, contaminants such as alkali metals, phosphorous compounds and the waxes, sterols, tocopherols and carotenoids contained in natural oils and fats can inhibit catalyst performance and may therefore need to be removed prior to processing [9–11].

Despite these concerns, to the knowledge of the authors, no research to date has been published on the effect of converting a sterol-rich microbial lipid into useable hydrocarbon fuels. Here, we investigated the effect of sterol content on the catalytic cracking of rapeseed oil over HY, HZSM-5 and Pd/C catalysts. To determine whether catalytic cracking could be used to provide a hydrocarbon fuel from a sterol-rich lipid feedstock, an unrefined yeast oil derived from the oleaginous yeast *Metschnikowia pulcherrima* was also subjected to catalytic cracking and the fuel properties of the resulting liquid product were assessed. The oil from *M. pulcherrima* was selected for this study as the yeast has been previously shown to grow on waste products and under inexpensive non-sterile conditions [35]. This yeast therefore offers a potential economic and sustainable source of lipid.

2. Experimental section

2.1. Materials

General lab solvents were purchased from Sigma–Aldrich and used without further purification. Deuterated chloroform ($CDCl_3$) for ^1H NMR analysis was purchased from Fluorochem. Winter-grade ultra-low sulphur diesel (ULSD-1) with 0% biodiesel was supplied by the Ford Motor Company. Rapeseed oil was purchased from a local supermarket (Co-operative group vegetable oil made from EU rapeseed) and contained 62% mono-unsaturates, 30% polyunsaturates and 8% saturated esters. Cholesterol (94%) was purchased from Sigma–Aldrich, UK. Yeast oil was extracted from *M. pulcherrima* according to literature methods [36]. All reagents were de-aerated and dried under standard Schlenk procedures before use. Three industrially relevant catalysts were selected for testing. Palladium on activated charcoal, (5% Pd basis) was purchased from Sigma–Aldrich, UK and used without further purification. Y zeolite was purchased as ammonium Y zeolite from Sigma–Aldrich with a SiO_2 to Al_2O_3 ratio of 5.02, and calcined at 550 °C for 3 h to generate the H^+ form, according to a procedure specified elsewhere [37]. Pelleted H^+-ion exchanged ZSM-5 zeolite (SiO_2 to Al_2O_3 ratio of 38) was purchased from ACS Material, US, crushed, sieved and vacuum oven-dried at 80 °C overnight. All catalysts were dried prior to use using standard Schlenk procedures. The crushed HZSM-5 and ammonium Y zeolite were both analysed by TGA prior to drying and calcination.

2.2. Methods

Conversion reactions were carried out in 50 mL batch reactors (Swagelok sample cylinder 304-L-HDF4-50, sealed with 1/4″ NPT plugs, SS-4-P, and a high temperature Sealant, MS-TL-SGT). The reactors were loaded under argon with 3 g of reactant and 0.5 g of catalyst. Heating was provided by a tubular pyrotherm furnace with a Eurotherm temperature controller. Reaction temperatures ranged from 300 °C to 400 °C, with a reaction time of 1 or 4 h, measured from the time the reactor was placed inside the pre-heated furnace. The temperature equilibrium for this set up is rapid, with no more than 5 min being needed to bring the reactor to