



Co-hydrotreating of algae and used engine oil for the direct production of gasoline and diesel fuels or blending components



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ABSTRACT

Co-hydrotreating of microalgae (M) and UEO (used engine oil) was examined for the direct production of gasoline and diesel fuels or blending components. The addition of the noble metal catalysts promoted the cracking and in situ hydrogenation of liquid products (oils) and was beneficial for the production of liquid products. Using Pt/C as the catalyst, the effects of temperature (350–450 °C), time (2–6 h), UEO/M mass ratio (6/0–0/6), catalyst loading (1–60 wt.%), and initial H₂ pressure (0.1–8 MPa) on the yield and quality of the liquid products were studied. A synergistic effect existed during the co-hydrotreating of the UEO and microalgae, which not only favored the production of liquid products but also promoted in situ denitrogenation and deoxygenation. Co-hydrotreating produced an upgraded oil with fuel properties (e.g., density, calorific value) comparable to traditional liquid transportation fuels derived from fossil fuel. The S content (45 ppm) of the upgraded oil produced at 450 °C is even below the minimum requirement of China IV diesel (50 ppm). Examination of the composition of the upgraded oils showed the formation of dominant light aliphatic and aromatic hydrocarbons that could also be used as a chemical feedstock.

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1. Introduction

Currently, crude oils are used to meet approximately 31.5% of the world's energy supply, and they supply approximately 80% of the feedstock used in chemical industries [1]. The economic development of newly industrialized countries such as China and India has greatly increased the demand for energy and petroleum products in recent decades, which will only continue to increase in the near future [2]. The excessive use of fossil fuels and the increase of energy accelerate the negative environmental impact, which includes global warming and fog and haze weather, in particular, in the north of China during the fall and winter seasons. Moreover, the current fossil fuels may be depleted by the year 2050 [3]. Therefore, a shortage of fossil fuels combined with environmental issues have stimulated the development of alternative energies.

Among these alternatives, biomass is a promising substitution for fossil fuels due to its high abundance, renewability, and carbon-

neutral character, and it is able to reduce or eliminate the negative effects associated with the use of fossil fuels [4,5]. Therefore, developing a biomass energy can solve the problem of energy scarcity and eradicate the increasing fog and haze pollution. Biomass can serve as liquid biofuel by subjecting it to different thermal, biological, and physical processes [6,7]. Liquid biofuels are important because they represent a renewable energy source that can be used to supplement our existing liquid fuel transportation system and vehicles. No other renewable fuel can be converted to a liquid for our current vehicles. Liquid biofuels can also be used to displace fossil heating oil in boilers (residential, commercial and industrial applications) in suburban and rural areas where natural gas for heating is not available. Thus far, various types of biomass feedstock have been tested for the production of biofuels [8]. Russo et al. [9] and Lawlor and Olabi [10] reviewed the state-of-the-art for pure plant oil (PPO), tallow and RVO (recycled vegetable oil) used as fuel in diesel engines and suggested that they are good candidates to substitute a small to medium portion of petroleum, making a significant contribution as renewable fuel. In addition to the food and nonfood crops mentioned above, algae (in particular, microalgae) have demonstrated great potential due to their high lipid

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Nomenclature

Abbreviation

UEO	used engine oil
M	microalgae
Pt/C	platinum supported on carbon
Pd/C	palladium supported on carbon
Ru/C	ruthenium supported on carbon
Rh/C	rhodium supported on carbon
Ir/C	iridium supported on carbon
<i>C. pyrenoidosa</i>	<i>Chlorella pyrenoidosa</i>
db	dry basis
daf	dry ash free basis
ASTM	American Society for Testing and Materials
TGA	thermogravimetric analysis
GC–MS	gas chromatography-mass spectrometry
ER	energy recovery

Notations in formulation

<i>m</i>	mass, kg.
HHV	higher-heating value, MJ/kg.
TAN	total acid number, KOH mg/g
wt.%	weight percentage

content, high growth rate, and non-competition for arable land [11,12]. The harvested microalgae usually contain significant quantities of moisture, and thus aqueous-phase processing of such biomass feedstocks is attractive from an energy perspective. “Two-step” hydrothermal processes (liquefaction followed by catalytic hydrotreatment) was commonly used to treat microalgae for the production of high quality liquid biofuel [13,14]. However, challenges are accompanied by this “two-step” hydrothermal processes, that is, water would incorporate into the final bio-oil products, and thus increase the oxygenation content of the final bio-oil [14]. Moreover, this “two-step” process would also result in low yield of final bio-oil due to the multiple sample transfers that are required for separation of the product fractions and to the use of evaporation to remove solvents from the samples. Therefore, new and integrated processes are necessarily needed to be developed for biofuel recovery from the microalgae.

With the rapid development of the transportation industry in China, oily wastes (e.g., used engine oil, waste lubricant oil and oil sludge) gradually lead to extensive environmental problems. For both economic and environmental reasons, the utilization of waste, such as used engine oil, oil sludge, and bilge water, as an energy source has become important. Environmental regulatory authorities are increasingly concerned regarding the potential adverse impacts of the transportation industry. Based on the latest statistics, the transportation industry produces 25 million tons of UEO (used engine oil) each year in China [15]. If these hazardous waste products are discarded or handled improperly, it can lead to serious environmental pollution. As the rate of generation of these materials increases in today's modern society, the difficulty in disposing of waste is a significant problem [16]. One of the promising methods of obtaining profit in the energy value of these waste products is by recycling. UEO has a variable composition depending on the composition of the original oil and the degree of degradation. This material is a complex mixture of aliphatic, aromatic, and olefinic hydrocarbons, among which aliphatic hydrocarbons account for 99% [17]. Therefore, UEO is a potential solvent for in situ hydrotreating of the microalgae and do not necessarily need to be

separated from the product oil. Furthermore, the dispersing and clearing agents in the UEO are potential sources for the control of coke formation during the in situ upgrading of the oil intermediates.

Therefore, the objective of the current study is to explore the integrated in situ catalytic upgrading of microalgae and UEO. To the best of the authors' knowledge, this is the first research to examine the in situ catalytic upgrading of microalgae and UEO for the production of liquid fuel. First, the reaction of different potential catalysts for the in situ upgrade of the reaction products was examined. Subsequently, using the selected catalyst, the effects of the reaction temperature, time, UEO/microalgae mass ratio, catalyst loading, and initial H₂ pressure on the yields of the products fractions and the properties of the resulting liquid products were investigated. Lastly, the bulk properties (e.g., elemental composition and heating value) and the molecular characteristics (e.g., molecular constituents and functional group allocation) of the resulting liquid products (oil) were determined.

2. Experimental section

2.1. Materials

Five noble metals supported on activated carbon (Pt/C, Pd/C, Ru/C, Rh/C, and Ir/C) were obtained from Zhengzhou Alfachem Co., Ltd. and used as in situ upgrading catalysts. All of the catalysts were received in powder form and had an average particle size of 25 μm. They were directly mixed with the reaction slurry without undergoing a pre-reduction under H₂ prior to use. The relevant properties of the catalysts were determined experimentally, and the results are reported in Table 1.

C. pyrenoidosa (*Chlorella pyrenoidosa*), which was heterotrophically cultured in an open pond, was purchased from Shandong Binzhou Tianjian Biotechnology Co., Ltd. (North China) and received in dry powder form. The proximate and ultimate analysis of this microalga is available in a previous publication [14]. *C. pyrenoidosa* consisted of 7.2 wt.% moisture (dry basis, db), 9.2 wt.% ash (db), 15.5 wt.% fixed carbon (db), 90.0 wt.% volatile matter (dry ash free basis, daf), 20.6 wt.% lipid (dichloromethane soluble fraction, daf), 61.2 wt.% protein (daf), and 8.2 wt.% carbohydrates (calculated by difference). The major inorganic composition of the algae consisted of 1.17 wt.% Na, 0.40 wt.% Mg, 0.17 wt.% Al, 0.90 wt.% Si, 0.51 wt.% P, 2.76 wt.% Cl, 0.43 wt.% K, 4.44 wt.% Ca, 0.08 wt.% Mn, 0.07 wt.% Fe, 0.21 wt.% Sr, and 0.02 wt.% Mn. The UEO was obtained from a local automobile servicing station in Jiaozuo, Henan province (Central China). It contains 1.5 wt.% moisture and 0.15 wt.% ash. Its elemental compositions are listed in Table 2.

Freshly deionized water was used throughout the experiments. Hydrogen was commercially available with a purity ≥99.999%.

A custom-built high-pressure stainless-steel batch reactor with a total internal volume of 58 mL was used to perform the in situ upgrading experiments. Prior to its use in the experiments, the reactor was loaded with water and treated at 400 °C for 4 h to remove any residual organic material from the reactors and expose the fresh metal walls to the supercritical water. This conditioning

Table 1
Catalyst compositions.

Catalyst	Composition (from supplier)	BET area (m ² /g)	Metal dispersion (%)
Pd/C	Pd (5 wt.%)	888	39.4
Pt/C	Pt (5 wt.%)	419	5.4
Ru/C	Ru (5 wt.%)	966	23.2
Rh/C	Rh (5 wt.%)	980	21.0
Ir/C	Ir (5 wt.%)	861	11.0

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