



Catalytic partial oxidation of a biodiesel surrogate over molybdenum dioxide



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HIGHLIGHTS

- The light-off temperature of the CPO of methyl oleate over MoO₂ is 750 °C.
- CPO of methyl oleate over MoO₂ shows a carbon conversion > 95% at 850 °C.
- CPO of methyl oleate over MoO₂ shows near 50% of H₂ yield at 850 °C and O₂/C = 0.6.
- MoO₂ displays high coking resistance for long-chain oxygenated compounds.
- MoO₂ is stable under low pressure and high WHSV up to 10 h⁻¹.

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ABSTRACT

The generation of synthesis gas by catalytic partial oxidation (CPO) from renewable liquid fuels for solid oxide fuel cell applications has been the target of several studies. Typically, noble metals or nickel are employed as the active catalyst for fuel reforming, but they present drawbacks in terms of high cost and deactivation due to carbon deposition, respectively. Thermodynamically, the CPO of the model biodiesel compound, methyl oleate (C₁₉H₃₆O₂), was found to be favorable at temperatures > 800 °C. Under these conditions, we report a high catalytic activity of molybdenum dioxide (MoO₂) toward the reformation of methyl oleate into synthesis gas, while overcoming the disadvantages of coking and methane formation. For an O₂/C molar ratio between 0.60 and 0.70 and a WHSV up to 10 h⁻¹, the CPO reaction shows a fuel carbon conversion above 80%, relatively good H₂ and CO yields, and the catalyst exhibits high redox stability. It is proposed that the lattice oxygen present in the oxide promotes the CPO reaction via the Mars–van Krevelen mechanism.

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1. Introduction

In recent years, there has been special attention to designing a highly integrated propulsion/airframe system with multiple distributed power sources for maximizing fuel efficiency while reducing noise and emission of greenhouse gases from airplanes such as NO_x, CO_x and unburned hydrocarbons [1–3]. One way to achieve this goal is by introducing the concept of the “More Electric Airplane” (MEA) into future designs [4,5]. This implementation involves increasing the use of power electronics in the starter/generation system of the main engine while removing the need for

on-engine hydraulic power generation and bleed air off-takes [6,7]. These changes would play an important role in increasing the lifetime of the main drive engines. One option to implement the MEA concept involves solid oxide fuel cells (SOFCs) that harness the efficient electrochemical fuel combustion reaction to generate electrical energy. For instance, Boeing has considered replacing the inefficient conventional gas turbine auxiliary power unit (APU) with a fuel cell based APU to provide the required electrical power during ground operation, and to reduce the shaft of extractions of the main engine during the idling, taxi, climb, cruise and descent segments of the flight [2,8]. However, the lack of a hydrogen infrastructure at existing airports and the limitations of a suitable hydrogen storage technology requires the fuel cell system to be integrated with onboard fuel reformers. In these systems,

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Jet-A (a standard kerosene-based aviation fuel) would be catalytically converted into synthesis gas (a mixture of H_2 and CO) [9] that would be subsequently fed into the SOFC.

Additionally, the current aircraft industry demands sustainability. In this regard, the use of renewable resources will contribute to reducing polluting gases, decreasing the dependence of energy imports, and promoting local and regional economies [10–12]. Biodiesel – a non-toxic and biodegradable mixture of long chain fatty acid methyl esters made by transesterification of vegetable oils and animal fats – represents a prospective liquid transportation fuel with high potential to replace diesel and Jet-A fuel in the future with 60% less net-life cycle carbon dioxide emissions [13–15]. As a demonstration of this potential, a Honeywell corporate Jet was successfully flown using a 50:50 blended Green Jet fuel and a standard Jet-A fuel mixture from Morristown (New Jersey) to Paris – Le Bourget Airport in 2011 [16]. Furthermore, as with other liquid fuels, biodiesel could be employed in a fuel cell system where it is pre-fed into an external reformer to produce synthesis gas. Nevertheless, at this time, the state of the art for the catalytic partial oxidation (CPO) of oxygenated molecules for the production of synthesis gas relies mainly on light alcohols such as methanol or ethanol [11].

Moreover, molybdenum dioxide (MoO_2) has been recently explored in CPO reactions of different logistic fossil fuels such as gasoline and Jet-A [17–20] where their main composition are represented by a mixture of hydrocarbons (linear and branched paraffins, cycloalkanes and aromatics) [9]. Here, we report that MoO_2 can be also employed as a catalytic material for the CPO of biodevised oxygenated complex liquid fuels such as biodiesel to produce syngas, while minimizing the intrinsic problem of coking.

Therefore, the present work focuses on the generation of synthesis gas from biodiesel reforming via a CPO route. This study will provide new insights for reforming complex oxygenated fuels, in which coke formation might become a considerable issue because of the inherent tendency of biodiesel to form carbonaceous species due to their long hydrocarbon chain and thermal instability at high temperatures [11,21]. Thus, in a long-term run, nickel-based catalysts cannot be considered as a suitable option owing to their well-known propensity to form graphitic carbon, whereas the use of noble metal (e.g., Ru, Rh, Pd, Pt or Ir) catalysts is not economically feasible.

2. Materials and methods

Commercial unblended B100 canola-soy biodiesel was acquired from Imperium Renewables (Seattle, WA). The weight composition of this commercial biodiesel was obtained from a gas chromatograph – mass spectrometer (GC–MS) and is given in Table 1. Based on these results, methyl oleate ((Z and E) – 9 – octadecenoic methyl ester) represents the main component of the canola biodiesel.

Table 1
Chemical analysis of canola biodiesel from Imperium Renewables.

Main Components	Global Formula	% in Weight
Hexadecanoic acid methyl ester	$C_{17}H_{34}O_2$	2.914
9,12 – Octadecadienoic acid (Z,Z) – methyl ester	$C_{19}H_{34}O_2$	11.909
9 – Octadecenoic acid – methyl ester ^a	$C_{19}H_{36}O_2$	59.327
Octadecanoic acid methyl ester	$C_{19}H_{38}O_2$	2.657
11 – Eicosenoic acid methyl ester	$C_{21}H_{40}O_2$	0.731
Eicosanoic acid methyl ester	$C_{21}H_{42}O_2$	0.399
Docosanoic acid methyl ester	$C_{23}H_{46}O_2$	0.178

^a Z and E compounds.

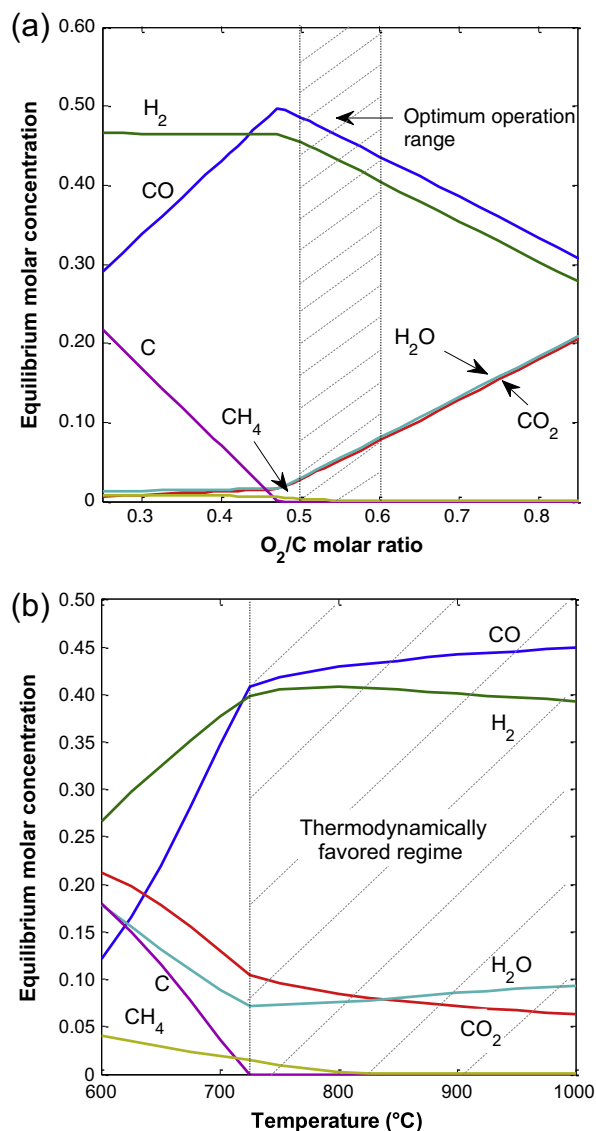


Fig. 1. Thermodynamic analysis of the CPO of methyl oleate at atmospheric pressure. (a) The effect of the O_2/C molar ratio on the gas molar composition at 850 °C under equilibrium conditions. (b) The effect of the temperature on the gas molar composition at a fixed O_2/C ratio of 0.6.

sel, and was thus chosen as its surrogate for the reforming reaction. Methyl oleate is usually derived by transesterification of triolein, the triglyceride of oleic acid [14].

Physical characterization of molybdenum dioxide (MoO_2 , Alfa Aesar, CAS No. 18868-43-4) was performed on a Micromeritics 3020 TriStar II automatic physisorption analyzer with N_2 at -196 °C. The specific surface area was calculated based on the Brunauer–Emmett–Teller (BET) method. The sample was degassed at 200 °C under vacuum for 1 h prior the measurement. Also, fresh and spent samples were characterized by powder X-ray diffraction (XRD) using a PanAnalytical X'Pert Pro Ray unit (model MPD 3040), The X-ray source was a Co anode ($K\alpha = 0.179$ nm) operated at 40 kV and 45 mA. Diffraction patterns were recorded within the 2θ range of 20–100° with a step width of 0.01673° and a dwell time of 2 s. In the case of nickel powder (Ni, Alfa Aesar, CAS No. 7440-02-0), a pre-reduction process at 450 °C with 30 sccm of H_2 (ultra high purity grade) for 2 h was implemented prior to the catalytic reaction.

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