



Quality and sustainability comparison of one- vs. two-step catalytic hydroprocessing of waste cooking oil



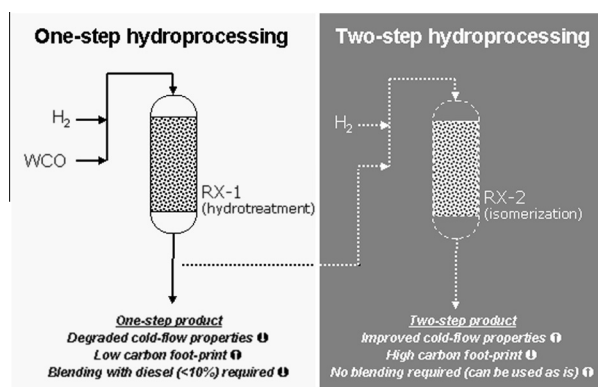
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HIGHLIGHTS

- One- and two-step catalytic hydroprocessing of waste cooking oil renders high quality fuels.
- High cold flow properties (e.x. CFPP) is only drawback of one-step approach diesel.
- CFPP limitation is addressed by a second isomerization step or blending with fossil diesel (<10%).
- One-step product blends with fossil diesel have lower carbon footprint product abiding by EN590.

GRAPHICAL ABSTRACT



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ABSTRACT

A quality and sustainability comparison of the catalytic hydroprocessing of waste cooking oil (WCO) using a single-step (hydrotreatment) vs. a two-steps (hydrotreatment + isomerization) approach was conducted. The product fuel properties from both approaches were excellent, abiding by the newly established CEN TS 15940:2012 standard for Hydrotreated Vegetable Oil (HVO) fuels. The only consideration of the single-step product regarding its increased cold flow properties was addressed by the second isomerization step or by blending with fossil diesel (<10% v/v). Furthermore, the environmental impact of the examined one- and two-step WCO catalytic hydroprocessing was evaluated via Life Cycle Assessment (LCA), quantifying the associated greenhouse gas (GHG) emissions. LCA indicated a reduced sustainability of the two-step product as compared to the one-step product, due to the additional energy and hydrogen requirements of the second isomerization step.

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1. Introduction

The conventional petroleum-based fuels contribute significantly to the industrial growth and technological development, constituting a prominent source of transportation energy. However, the limited sources of these fuels are consecutively depleting,

since their consumption is rapidly increasing. Moreover, the production and use of petroleum fuels have generated considerable and potentially irreversible environmental problems, including global warming. Consecutively, it became important to identify sustainable and environmentally friendly fuels, leading to the recent advances in the area of biofuels [1,2].

Biofuels are fuels derived from biomass conversion, and can be classified as solid biofuels, liquid biofuels and various bio-gases. Biofuels are gaining increased public and scientific attention, impelled by factors such as oil price increments, the necessity for renewable energy sources and environmental considerations [2].

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By far the most common biofuel within the European Union is FAME (Fatty Acid Methyl Esters) biodiesel produced via the transesterification of vegetable oils [1,3]. Nevertheless, the production of FAME has raised major concerns about the associated feedstocks' origin and their competition with food crops [4].

Apart from transesterification, an alternative conversion process of vegetable oils into biofuels is catalytic hydroprocessing. Catalytic hydroprocessing constitutes a modern way to produce premium quality bio-based diesel fuels, that are also referred to as “renewable diesel fuels” instead of the term “biodiesel”, which has prevailed for FAME. In industrial scale, Hydrotreated Vegetable Oils (HVOs) are produced from vegetable oils and/or grease by Universal Oil Products (UOP) (product's trade name green diesel) [5] and from vegetable oils and/or animal fats by NesteOil Corporation (product's trade name NExBTL- acronym for “Next Generation Bio-to-Liquid”) [6]. As far as UOP is concerned, the Ecofining process is employed, which is an integrated two-stage hydrorefining process. The first step includes catalytic hydrodeoxygenation process producing a paraffin-rich product that is then submitted to a second step of catalytic hydroisomerization resulting to a high quality renewable diesel fuel [5]. The NExBTL of NesteOil is also the product of two consecutive steps, hydrotreatment and isomerization [6].

As both aforementioned industrial production processes of HVOs indicate, it is necessary to include two catalytic hydroprocessing steps. The first step of hydrotreatment converts the triglycerides of the lipid feedstock into an oxygen-free hydrocarbon-based fuel consisting of primarily normal paraffins, which even though has an impressively high cetane number, it also has degraded (high) cold flow properties. The product of the first step then undergoes a second hydroprocessing step where isomerization/dewaxing enables the conversion of normal paraffins into iso- and cyclo-paraffins, leading to an improved fuel with sufficiently low cold flow properties (20–30 °C lower than that of the product of the first hydroprocessing step) [6].

Several research activities in laboratory- and pilot-scale have also targeted on optimizing lipids conversion via catalytic hydroprocessing, most of which however have focused on the first hydrotreatment step [7–9]. The catalytic hydrotreatment of residual lipids such as waste cooking oil (WCO) was also examined [10], including the authors' previous work [11–14] which is extensively discussed in Section 2.4. WCO has significant sustainability potential as a residual biomass that does not compete with food production, while its reuse can impede environmental problems raised from their disposal [15]. The resulting fuel is a mixture of paraffinic hydrocarbons, free of sulfur, oxygen and aromatics, thus fully compatible with fossil fuels as all HVOs. The hydrotreated WCO fuel exhibits superior characteristics including high cetane number, increased oxidation stability, high heating value and negligible acidity and water content [16]. The single step hydrotreatment has increased cold flow properties due to the paraffinic content of the product, which requires dewaxing/isomerization. However, only limited work exists on the isomerization of the paraffins produced via catalytic hydrotreatment of lipids, mainly focusing on the development of new catalytic material enabling dewaxing [17,18]. Based on these two studies, the second isomerization step can reduce the CFPP of HVOs from +23 °C down to –5 °C to –15 °C.

Apart from the technical aspects regarding the production of renewable bio-based diesel fuels, the greenhouse gas (GHG) emissions connected with their production processes receive considerable attention nowadays. This is a main challenge regarding biofuels in order to meet the increasing energy requirements, by employing the most sustainable approach which minimizes the associated GHG emissions. The environmental impacts of biofuels are commonly evaluated via a Life Cycle Assessment (LCA) analysis that constitutes a valuable tool identifying the environmental

merits and demerits of a product system throughout its life cycle, and is included in studies aiming to increase energy efficiency and sustainability. Specifically, LCA analysis provides data on the environmental impacts of an examined production process, by quantifying the associated GHG emissions [19]. LCA analysis has been applied for the assessment of the environmental performance of Hydrotreated Vegetable Oils (green diesel and NExBTL product) [5,19], as well as other biofuels [20–23].

As WCO is the most sustainable feedstock that can be employed for renewable diesel production, this paper focuses on comparing the one- vs. the two-step hydroprocessing of WCO regarding their quality and sustainability characteristics. Initially, WCO was subjected to a first catalytic hydrotreatment step by using a commercial NiMo hydrotreating catalyst and then the liquid product is further processed via a second hydroisomerization step, using a commercial isomerization catalyst. In addition, the environmental impacts of the one- and two-step hydroprocessing of WCO were assessed via LCA, to determine the carbon footprint of each product.

2. Materials and methods

2.1. Feedstocks and catalysts

WCO was the only feedstock used in this study, collected from local restaurants and households, the properties of which are given in Table 1. The composition of WCO includes 7.46% palmitic acid (C16:0), 2.97% stearic acid (C18:0), 33.52% oleic acid (C18:1) and 54.79% linoleic acid (C18:2), while a more detailed analysis is described in the authors' previous work [12]. No pretreatment step was included besides filtration via a regular sieve to remove leftover food particles and frying residues.

WCO was the feedstock for the first step of catalytic hydroprocessing, the product of which constituted the feedstock for the second isomerization step. For the first hydroprocessing step a commercial Haldor-Topsøe NiMo/ γ -Al₂O₃ was utilized, typical for gasoil hydrotreatment. This sulfided catalyst was selected as it offers dual functionality enabling hydrogenation and hydrogenolysis of C–C bonds. The hydrogenation function enables heteroatom removal and saturation of double bonds, which is indicated by the significantly decreased sulfur, nitrogen and oxygen content of the product after the single hydroprocessing step, as well as the as from the Bromine index drop presented in Table 1. For the second step another commercial Haldor-Topsøe catalyst was employed suitable for paraffin isomerization. This isomerization catalyst has a low amount of zeolite and high load of NiW, rendering it with high (de)hydrogenation activity and relatively low acidity (compared with catalysts with higher load of zeolites). It should be noted that in order to control the catalyst activity, dimethyl disulfide (DMDS) was added to the feedstocks of both reaction steps, as recommended by the manufacturer. The sulfur added as DMDS is easily retrieved as H₂S in the gaseous product (see Table 2).

The reactor loading was a critical first step, as it had to be conducted in an efficient way to ensure homogeneity in both radial and axial directions. In order to maintain the desired Liquid Hourly Space Velocity (LHSV), a particular catalyst amount was employed, which is diluted with an inert material (silicon carbide) to ensure that it would be effectively dispersed throughout the reactor to achieve good heat and mass transfer while enabling feed channeling. Before the beginning of each experiment, each catalyst was pre-sulfided *in-situ* according to the procedure defined by the catalyst manufacturer. Once the catalyst was pre-sulfided, the feedstock was introduced and the experiment began.

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