

Fuel properties of hydroprocessed rapeseed oil

Pavel Šimáček^{a,*}, David Kubička^{b,1}, Gustav Šebor^a, Milan Pospíšil^a

^aInstitute of Chemical Technology, Prague Department of Petroleum Technology and Alternative Fuels, Technická 5, 166 28 Prague 6, Czech Republic

^bResearch Institute of Inorganic Chemistry, Department of Refining and Petrochemical Research, 436 70 Litvínov – Záluží 1, Czech Republic

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ABSTRACT

This paper deals with the hydroprocessing of rapeseed oil as a source of hydrocarbon-based biodiesel. Rapeseed oil was hydroprocessed in a laboratory flow reactor under four combinations of reaction conditions at temperatures 310 and 360 °C and under hydrogen pressure of 7 and 15 MPa. A commercial hydrotreating Ni–Mo/alumina catalyst was used. Reaction products contained mostly *n*-heptadecane and *n*-octadecane accompanied by low concentrations of other *n*-alkanes and *i*-alkanes. Reaction product obtained at 360 °C and 7 MPa was blended into mineral diesel fuel in several concentration levels ranging from 5 to 30 wt.%. It was found, that most of the standard parameters were similar to or better than those of pure mineral diesel. On the other hand, low-temperature properties were worse, even after addition of high concentrations of flow improvers.

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1. Introduction

Hydroprocessing of vegetable oils allows easy transformation of fatty acid triglycerides into hydrocarbons. Three most important reactions take place during hydroprocessing of vegetable oil [1]:

- (i) Hydrogenation of double bonds present in unsaturated chains of bonded fatty acids.
- (ii) Hydrodeoxygenation (HDO), which results in removal of oxygen atoms from carboxylic group in the form of water.
- (iii) Hydrodecarboxylation (HDC), which leads to elimination of carboxylic group in the form of carbon dioxide.

It was found that hydrogenation of double bonds precedes HDO and HDC reactions [1]. HDO and HDC of saturated triglycerides proceed at different reaction rates, which depend on reaction conditions and type of catalyst used. The changes in the respective reaction rates can be observed by the changing ratio of the principal products, *i.e.* *n*-octadecane in the case of HDO and *n*-heptadecane in the case of HDC. In general, the main reaction products of vegetable oil hydroprocessing are thus *n*-alkanes having the same carbon atom number as fatty acids present in the original vegetable oil (HDO) and *n*-alkanes with the carbon atom number lower by one as compared to the carbon atom number of fatty acids in the original vegetable oil (HDC). Hydroprocessing of common veg-

etable oils (rapeseed, sunflower, soybean and palm oil) leads to hydrocarbon mixtures, in which *n*-alkanes C₁₅ to C₁₈ are predominant [2–4].

Reaction conditions and type of catalyst also influence the extent of side reactions leading to formation of *i*-alkanes, cycloalkanes and aromatics [2,4]. Cracking of the hydrocarbon chains is usually negligible. The vegetable oil hydroprocessing [5] is sometimes referred to as hydrogenation [6] or hydrocracking [2,3]. However, the term hydrogenation can be misleading, because it has a different meaning in food industry. During this process the unsaturated chains of fatty acids are hydrogenated and become saturated while the structure of triglycerides remains unchanged. The term hydrocracking may also not be completely exact, because cracking of carbon–carbon bonds occurs only in some cases (HDC) and generally at the carbon atom carrying oxygen-functional group. Therefore, we will denote the set of reactions in this reaction system as hydroprocessing and the individual reactions will be referred to as hydrodeoxygenation (HDO) and hydrodecarboxylation (HDC) throughout the article.

From the refinery point of view, all hydrocarbons present in hydroprocessed vegetable oil belong to middle distillates and are thus suitable for production of diesel fuel. Hydroprocessed vegetable oil can be, hence, called hydrocarbon-based or oxygen-free biodiesel. Oxygen-free biodiesel eliminates some drawbacks of the traditional FAME-type biodiesel relating mostly to fuel stability. Car manufacturers would probably also prefer hydrocarbon-based biodiesel to FAME as it offers full compatibility with current diesel fuel for which the diesel engine systems are optimized. Moreover, the content of such bio-component in diesel fuel could be much higher than 5 vol.% permitted currently for FAME concentration

* Corresponding author. Tel.: +420 220 444 236; fax: +420 220 444 321.

E-mail addresses: pavel.simacek@vscht.cz (P. Šimáček), david.kubicka@vuanch.cz (D. Kubička).

¹ Tel.: +420 476 163 735; fax: +420 476 768 476.

in diesel in Europe without negative impacts on engine operation. Thanks to its high content of *n*-alkanes, oxygen-free biodiesel has an excellent cetane number ranging from 55 to 90 [5] depending on degree of branching. The worsened low-temperature properties seem to be the only disadvantage in comparison with FAME-type biodiesel. Low-temperature properties can be improved either by choice of proper catalyst and reaction conditions or by isomerisation [7,8] following the hydroprocessing. It is also possible to use existing refinery technologies for co-processing of vegetable oil and petroleum feedstock. The most promising way is perhaps the addition of vegetable oil into feedstock for hydrocracking or hydro-treating [9,10].

Commercial production of hydrocarbon-based biodiesel from vegetable oil has been recently incorporated in petroleum refinery. Finnish company Neste Oil operates two vegetable oil hydroprocessing units with capacity 170 kt/y each in its refinery in Porvoo. Two world-scale plants, in Singapore and Rotterdam, with capacity 800 kt/y each are under construction [8,11,12]. The production of biodiesel takes place in two stages. Product of vegetable oil hydroprocessing (stage 1) proceeds to an isomerisation unit (stage 2) where its low-temperature properties are improved. The final product called NExBTL is used as renewable component for production of diesel fuel. Neste Oil guarantees that its Neste Green diesel, which suits all diesel engines, contains at least 10% of NExBTL.

The paper summarizes some fuel properties of hydroprocessed rapeseed oil obtained at various reaction conditions using commercial Ni–Mo catalyst. Furthermore, fuel properties of mixed fuels containing the selected hydroprocessed rapeseed oil (5–30 wt.%) and mineral diesel are reported and discussed. This work is a logical continuation of the recent experiments aimed at reaction mechanism description and determination of detailed composition of reaction products [4,13].

2. Experimental

2.1. Hydroprocessing

Hydroprocessing of rapeseed oil was performed in a bench scale flow reactor equipped with a salt bath heating system. The experimental set-up is schematically depicted in Fig. 1. All the feed and product lines were heated to prevent feed and product solidification in the lines. The liquid products were stripped with hydrogen

prior to sample collection (not shown in Fig. 1). The dimensions of the reactor were 900 mm (length) and 40 mm (inner diameter). The total amount of the catalyst used was 100 g. The composition of the commercial hydrotreating Ni–Mo/alumina catalyst was as follows: NiO – 3.8 wt.%, MoO₃ – 17.3 wt.% and P₂O₅ – 6.7 wt.%. Rapeseed oil used as raw material had food quality (S: 3 mg kg⁻¹; P: <0.5 mg kg⁻¹; Na: 5 mg kg⁻¹; K: 2 mg kg⁻¹; Ca: 4 mg kg⁻¹; Mg: <0.5 mg kg⁻¹). The liquid feed flow and hydrogen flow was 100 g h⁻¹ and 0.1 Nm³ h⁻¹, respectively. The WHSV and gas-to-oil ratio were thus 1 h⁻¹ and 920 Nm³/Nm³, respectively. The reaction products were collected during the hydroprocessing of rapeseed oil at two temperature levels, 310 and 360 °C, and at two hydrogen pressure levels, 7 and 15 MPa.

2.2. Analysis of products

After separation of aqueous and organic phases, the reaction products were analyzed by gas chromatography. A gas chromatograph, model HP-6890 (Agilent), was used for all chromatographic measurements. Gaseous products and all organic liquid products were analyzed by gas-chromatographic methods proposed in recent work [4]. Physicochemical properties of the organic liquid products and mixed fuels were determined using standard test procedures designated for diesel fuel or petroleum products.

2.3. Mixing of product with mineral diesel fuel

Organic liquid product (OLP) obtained by hydroprocessing of rapeseed oil at 360 °C and 7 MPa was chosen for preparation of blends with mineral diesel fuel. The mineral diesel fuel was obtained from a refinery and it had low sulfur content (10 mg kg⁻¹). Furthermore, it did not contain FAME or any additives. All monitored physicochemical properties of this basic mineral diesel corresponded to the properties of a commercial diesel fuel before final addition. Four diesel blends containing 5, 10, 20 and 30 wt.% of OLP, respectively, were prepared and evaluated as commercial diesel fuel according to the European standard EN 590. These mixed fuels were then separately treated with flow improvers Keroflux® 3566 (BASF) and Infineum R 288 (Infineum) in concentration ranges of 10–500 mg kg⁻¹ to evaluate their impact on low-temperature properties of the blends.

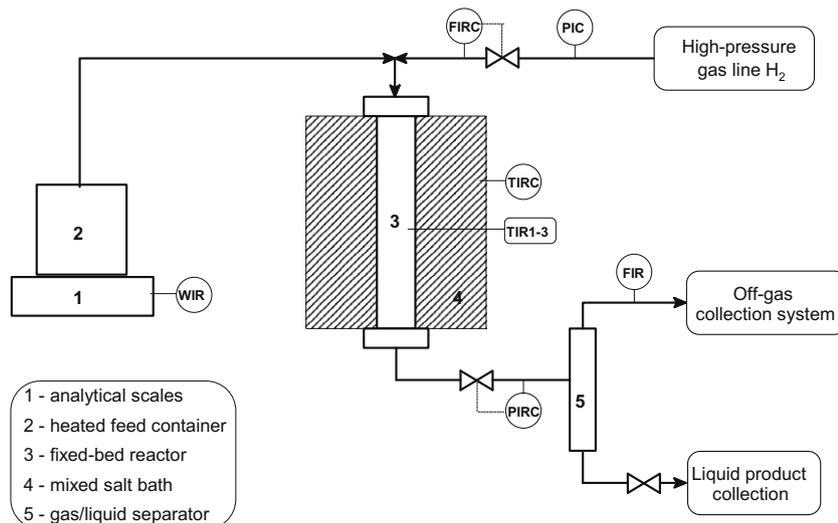


Fig. 1. A schematic figure of the bench scale reactor.

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