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Premium quality renewable diesel fuel by hydroprocessing of sunflower oil

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ABSTRACT

Hydroprocessing of neat sunflower oil was carried out at 360–420 °C and 18 MPa over a commercial hydrocracking catalyst in a bench scale fixed bed reactor. In the studied experimental range, products consisted exclusively of hydrocarbons that differed significantly in composition. While the concentration of *n*-alkanes exceeded 67 wt.% in the reaction products collected at 360 °C, it decreased to just 20 wt.% in the product obtained at 420 °C. Consequently, the fuel properties of the latter product were very similar to those of standard (petroleum-derived) diesel fuel. Particularly, it exhibited excellent low-temperature properties (cloud point −11 °C; CFPP −14 °C). Reaction products obtained at 400 and 420 °C were blended into petroleum-derived diesel fuel in three concentration levels ranging from 10 to 50 wt.% and the fuel properties of these mixtures were evaluated. Diesel fuel mixtures containing the product of sunflower oil hydrocracking at 420 °C showed very good low-temperature properties including cloud point (−8 °C) and CFPP (−15 °C) that was further lowered to −25 °C due to addition of flow improvers.

1. Introduction

Traditional biodiesel (fatty acid methyl esters – FAME) is produced from vegetable oils by homogeneously-catalyzed transesterification with methanol [1]. Even though FAME is suitable for blending with petroleum-derived diesel fuels, it suffers from some drawbacks, the main being low oxidation stability that limits (i) its long-term storage and (ii) the use of biodiesel–diesel blends containing more than 20–30 vol.% of FAME. Hydroprocessing of vegetable oils, i.e. their conversion into hydrocarbons resulting from their reaction with hydrogen at elevated temperature and pressure in the presence of heterogeneous catalysts, provides an alternative for diesel fuel production from renewable resources [2]. In contrast to FAME, hydrocarbons obtained by vegetable oil hydroprocessing are significantly more resistant to oxidation than FAME. Although the composition of products of vegetable oil hydroprocessing depends on several factors (reaction conditions, catalyst used), they can be in general characterized as low-aromatic sulfur-free hydrocarbon mixtures containing neither alkenes nor heteroatoms [2–9].

The fatty acids bound in vegetable oils have exclusively straight chains with an even number of carbon atoms. Consequently, their hydroprocessing yields *n*-alkanes as primary products. Two kinds of *n*-alkanes are formed: (i) *n*-alkanes that have the same carbon atom number or (ii) *n*-alkanes that have one carbon atom less than the original fatty acids present in vegetable oil [4,10–16]. Since fatty acids in natural vegetable oils have predominantly 18 carbon atoms in their chain, hydroprocessed vegetable oil often yields *n*-alkanes with high concentration of *n*-heptadecane and *n*-octadecane. The sum of these two hydrocarbons commonly reaches 70–90 wt.% [6–8]. These hydrocarbons have an excellent cetane rating, but their low-temperature properties are poor and prevent their direct use as a diesel fuel blending component in concentrations higher than 5–10%.

The subsequent reactions of primary hydrocarbon products, *n*-alkanes, lead to formation of other hydrocarbons: *i*-alkanes, cycloalkanes and aromatics. While the formation of aromatics is limited, several studies have demonstrated that with increasing reaction temperature the yield of *i*-alkanes increased significantly [6,17–20]. Higher reaction temperature favored also cracking reactions leading to the formation of light hydrocarbons in gasoline range [9] or even gases [14].

As mentioned above, the hydroprocessed vegetable oil has generally poor low-temperature properties. Cloud point and cold filter plugging point (CFPP) values of the products are usually higher than +20 °C [5,7,18]. Utilization of such fuel in moderate climate is impossible. It has been found that diesel fuel containing hydroprocessed rapeseed oil (5–30 wt.%) had significantly worse low-temperature properties than neat petroleum-derived diesel fuel. Moreover, the addition of flow improvers to these blends was inefficient, as it virtually did not affect their cold flow properties [7].

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The low-temperature properties of hydroprocessed vegetable oil can be upgraded by subsequent catalytic isomerization of *n*-alkanes. Hancsók et al. [18] have isomerized hydroprocessed sunflower oil using Pt/HZSM-22/Al_2O_3 catalyst. While the original CFPP of hydroprocessed sunflower oil was +23 °C, it dropped down to −23 °C after isomerization. Isomerization of the primary hydrocarbon products allowed commercial utilization of hydroprocessed vegetable oil as a new kind of renewable diesel fuel. At present, Neste Oil uses its product called NExBTL [19] not only as a component for diesel fuel blending, but even as a premium 100% renewable diesel fuel under the name Neste Green 100 diesel [20].

This paper focuses on determination of the composition and physicochemical properties of hydroprocessed sunflower oil obtained at four temperature levels. In contrast to the recent work concerning rapeseed oil hydroprocessing [7], different type of catalyst and more severe reaction conditions have been used in an attempt to prepare a hydrocarbon-based product having more favorable low-temperature properties. The properties of fuel blends consisting of petroleum-derived diesel (50–90 wt.%) and 10–50 wt.% of two selected hydroprocessing products are reported as well.

2. Experimental

2.1. Hydroprocessing

Hydroprocessing of sunflower oil was carried out in a bench scale fixed bed reactor equipped with a salt bath heating system. Dimensions of the reactor were 900 mm (length) and 40 mm (inner diameter). A commercial hydrocracking catalyst consisting of supported metal sulfides was used in the experiments. The catalyst was activated prior to the experiments using refinery recycle gas, i.e. hydrogen gas containing H_2S, at 360 °C and 18 MPa. The catalyst bed consisted of 70 g of the catalyst and 100 ml of silicon carbide that was used for catalyst bed dilution to minimize the wall effects and feedstock channeling. All experiments were performed under the hydrogen pressure of 18 MPa. The reaction products were collected at four temperature levels: 360, 380, 400 and 420 °C. The temperature range was chosen to convert triacylglycerides exclusively to hydrocarbons and to minimize their overcracking to light products. Liquid feed flow (sunflower oil) and hydrogen flow was 49 g h^{-1} and 0.049 N m^3 h^{-1}, respectively. Food grade sunflower oil was used as raw material.

2.2. Analysis of products

Organic liquid products and water were separated after pressure reduction from gas stream in a low pressure separator. After liquid sample collection, the organic liquid product was separated from water formed due to deoxygenation of the sunflower oil, i.e. due to its hydrodeoxygenation or due to hydrogenation of CO_2 originating from sunflower oil (hydro)decarboxylation. The gaseous products and water were not further analyzed. The composition of the organic products was then determined using gas chromatography (GC) and high performance liquid chromatography (HPLC). Simulated distillation and a conventional GC method were used for determination of distillation range and *n*-alkane content in the products, respectively. The detailed description of both GC methods has been reported recently elsewhere [16]. The content of aromatic hydrocarbons was determined using a standard HPLC method designated for diesel fuels (European standard EN 12916). These measurements were performed using a chromatographic set Shimadzu consisting of a pump (LC-10A), a control module (CBM-10A), a refractometric detector (RID-10A) and an oven (CTO-10AC) equipped with the column Supelcosil LC-NH2-NP (25 cm × 4.6 mm i.d.; particle size 5 μm). The flow rate of the mobile phase (*n*-heptane) was 1 cm^3 min^{-1}. The concentration of the sum of *i*-alkanes and cycloalkanes was balanced to 100%. Physicochemical properties of the neat hydroprocessing products as well as the properties of all prepared fuel blends were determined using the standard test procedures designated for diesel fuels (as defined by the European standard EN 590) or petroleum products (standards EN 12634 and EN ISO 3016). The cold filter plugging point (CFPP) of the hydroprocessing product obtained at 420 °C was measured also after treatment using flow improvers Infineum R288 and Infineum R591 in the concentration range of 200–800 mg kg^{-1}.

2.3. Preparation of fuel blends

The hydroprocessing products obtained at 400 and 420 °C were used for preparation of their fuel blends with petroleum-derived diesel fuel. FAME- and additive-free diesel was prepared in the laboratory by blending hydrotreated gas oil and kerosene in a weight ratio of 65:35. Low-temperature properties of the resulting diesel fuel corresponded to those of a commercial diesel fuel before the final addition of additives. The prepared petroleum-derived diesel was then blended with the hydroprocessing products in order to prepare six blends containing 10, 30 and 50 wt.% of the product obtained at 400 and 420 °C, respectively. The properties of these fuel blends were evaluated as a commercial diesel fuel according to the European standard EN 590. Finally, the fuel blends were separately treated with flow improvers Infineum R288 and Infineum R591 in the concentration range of 100–400 mg kg^{-1} to evaluate the efficiency of these flow improvers.

3. Results and discussion

3.1. Composition of reaction products

The chromatographic fingerprints of all products obtained by hydroprocessing of sunflower oil are presented in Fig. 1. There were not detected any oxygenated intermediates (such as fatty acids or fatty esters) in the reaction products. This observation is in agreement with previous findings [7]. Moreover, the absence of free fatty acids was indirectly confirmed by the low values of acid number of all products (see below). All products of sunflower oil hydroprocessing can be thus considered as neat hydrocarbon mixtures. It can be also clearly seen that the content of *n*-alkanes in the products decreased with the increasing reaction temperature (Fig. 1 and Table 1). Besides isomerization and cyclization, the higher reaction temperature also resulted in higher yields of lower hydrocarbons due to the more intensive cracking of the primary hydrocarbon products (mainly C_{15}–C_{18} *n*-alkanes). Two primary products of hydroprocessing, *n*-heptadecane and *n*-octadecane, represented more than 50 wt.% of the product obtained at 360 °C (Table 1). The increase of the reaction temperature by 20 °C caused a relative decrease of their concentration in the hydroprocessing products by more than 50%. Consequently, the product obtained at 420 °C contained only 2.8 and 1.8 wt.% of *n*-heptadecane and *n*-octadecane, respectively (Table 1). The total concentration of *n*-alkanes in this product is fully comparable with the content of *n*-alkanes in petroleum-derived diesel used for preparation of the fuels blends (see Table 1). On the other hand, the content of other saturated hydrocarbons (*i*-alkanes and cycloalkanes) increased with the increasing reaction temperature. The yield of aromatics increased also with the increasing reaction temperature as a result of the enhanced rate of the cyclization reactions. The dehydrogenation reactions proceeded in spite of the high hydrogen pressure (18 MPa). While the content of aromatics in the hydroprocessing