EFFECT OF THE HYDROGEN TO FEEDSTOCK RATIO ON THE HYDROTREATING OF THE MIXTURE OF PETROLEUM MIDDLE DISTILLATES AND RAPESEED OIL

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The hydrotreating of vegetable oils and animal fats is a possible way to produce a high-quality renewable diesel fuel component. It can be produced by processing the bio-raw material in new units or by the co-processing of the renewable raw material together with the petroleum middle distillates in existing hydrotreating units. This work was focused on investigating the effect of the hydrogen to the feedstock ratio on the hydrotreating of a mixture of petroleum middle distillates and rapeseed oil in a weight ratio of 8:2 in a tubular fixed-bed reactor. The hydrotreating was performed using a sulfided Ni-Mo/Al_2O_3 catalyst, a temperature of 345 °C, a WHSV of 1.0 h^{-1}, a pressure of 4.0 MPa and a hydrogen to the feedstock ratio in the range of 120-600 $m^3 \cdot m^{-3}$. The hydrogen to feedstock ratio of 120 $m^3 \cdot m^{-3}$ was not sufficient to desulfurise the feedstock to the level of 10 $mg \cdot kg^{-1}$. On the contrary, increasing the hydrogen to feedstock ratio to above 240 $m^3 \cdot m^{-3}$ had no significant effect on the yield and quality of the obtained products. Therefore, the ratio of 240 $m^3 \cdot m^{-3}$ was considered as sufficient for the hydrotreating of the mixture of the petroleum middle distillates and rapeseed oil.

Keywords: hydrotreating; vegetable oil; sulfided catalyst; renewable diesel; hydrogen to feedstock ratio; co-processing

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1. Introduction

The production of a renewable component into diesel fuel from triglyceride-based feedstocks is nowadays realised in two ways. First, fatty acid methyl esters (FAME) are produced via the transesterification of triglyceride feedstocks with methanol (usually catalysed by sodium methoxide) and the product is known as a biodiesel. Second, the oxygen-free diesel component composed of alkanes, commonly called Hydrotreated Vegetable Oil or Hydrodeoxygenated Vegetable Oil (HVO) is produced via the hydrotreating of vegetable oils and animal fats. HVO is also called Hydrotreated Esters and Fatty Acids (HEFA), a renewable synthetic diesel or renewable paraffinic diesel fuel from the hydrotreatment. HVO production usually includes an isomerisation unit for the improvement of the low-temperature properties even towards an arctic diesel fuel grade [1,2].

The biggest producer of HVO in the world is Neste, its product is usually labelled as NExBTL. NExBTL is produced in refineries in Finland, the Netherlands, and Singapore. The total yearly capacity of these units is approximately 3 million tonnes of NExBTL [3]. Approximately 80 % of the production of the renewable products is based on waste and residue fats and oils, a smaller part is produced from palm oil and other vegetable oils [4]. The technology Ecofining developed by UOP/ENI produces HVO labelled as Green Diesel [5,6]. The Haldor Topsoe HydroFlex sustainable renewable fuel technology can produce jet fuel or HVO from different renewable feedstocks [2]. Vegan from Axens is another technology for producing renewable diesel and jet fuel via the hydrotreatment of a wide range of raw materials containing lipids [7]. The total yearly capacity of all the installed units is approximately 4.5 million tonnes of HVO. In addition, there are companies that co-process triglycerides raw materials with petroleum distillates such as Petrobras (Brazil), Cepsa (with several refineries in Spain), Preem (Sweden), Repsol (Spain) and British Petroleum (Australia) [8].

Intensive research is carried out to find new feedstocks for the HVO production like algae, bacteria and microbial oils. Algae-based liquid transportation biofuels represent an emerging field with great potential. Microalgae have significant growth rates and can be produced in non-arable places, avoiding undesirable competition for food and feed production [8,9]. However, a lot of research and innovation is still needed to achieve full deployment and good economies of scale to achieve commercial applications [1].

During the hydrotreating, hydrogen is used to remove oxygen from the triglyceride molecules, which form the basis of the vegetable oils and animal fats. It is generally accepted that the first step in hydrotreating triglycerides is the hydrogenation of the double bonds in their aliphatic chains (see Figure 1). The following hydrogenolysis of the ester bonds of saturated triglycerides results in three molecules of fatty acids and one molecule of propane. The fatty acids are finally decomposed into hydrocarbons via hydrodeoxygenation (HDO), hydrodecarboxylation (HDCx) and hydrodecarbonylation (HDCn) reactions [10-13].

During the HDO of fatty acids, oxygen is removed in the form of water and n-alkanes with the same number of carbon atoms as in the corresponding fatty acids are formed. HDCx removes oxygen from the fatty acids with the generation of CO_2. CO and water are formed as by-products in the case of the HDCn reaction. In both cases, the resulting n-alkanes have one carbon atom less than the corresponding fatty acids. The CO and CO_2 produced may react with hydrogen to form methane (Reactions 1-3).

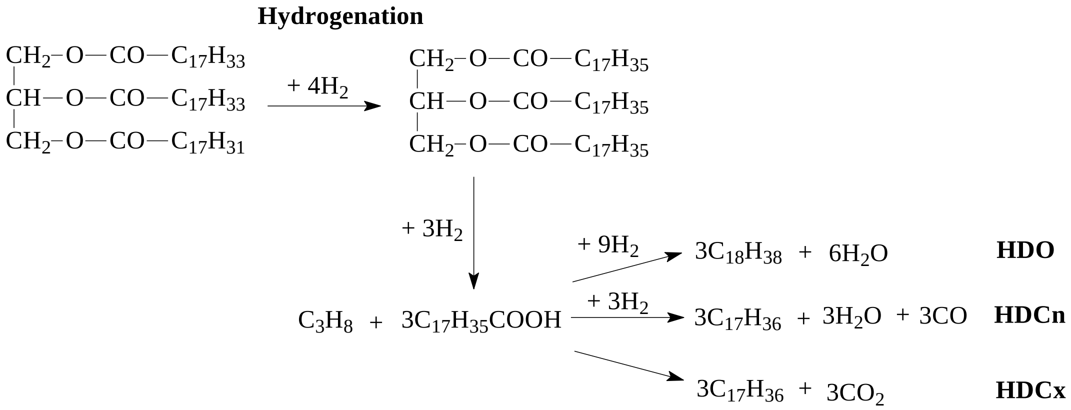

Fig. 1 The general reaction scheme of hydrotreating triglycerides

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (1)$$

$$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2 \quad (2)$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad (3)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (4)$$

Reverse water-gas-shift reaction (Reaction 4), together with methanation, limits use the amount of CO and CO_2 generated during the hydrotreating to determine the amount of the raw material that has been converted to the alkanes by HDCn and HDCx, respectively [10-13]. The extent of the hydrotreating reactions depends on the experimental conditions and the catalyst used.

Since the triglycerides present in most vegetable oils and animal fats mainly contain C_{16} and C_{18} acyls [8,11,14,15], a typical HVO mainly contains alkanes with C_{15}-C_{18} carbon atoms and is practically free of sulfur (< 5 $mg \cdot kg^{-1}$). The resulting n-alkanes can be transformed by isomerisation to isoalkanes. Cycloalkanes and aromatic hydrocarbons can be produced in small quantities by the cyclisation and dehydrocyclisation of alkanes. On a small scale, alkanes can be cleaved to alkanes with a lower number of carbon atoms [12,16].

The density of HVO (770–790 $kg \cdot m^{-3}$) is lower than that of fossil diesel fuel (820–845 $kg \cdot m^{-3}$ according to EN 590). HVO has a very high cetane number (> 70), low carbon residue on the 10 % bottoms remaining after distillation (< 0.1 wt%) and low viscosity at 40 °C (2-4 $mm^2 \cdot s^{-1}$). The boiling point at 95 vol% of the distillate is usually under 330 °C at the HVO distillation according to EN ISO 3405 which is lower than the one of fossil diesel fuel (≤ 360 °C according to EN 590). The low-temperature properties of HVO can be improved by the isomerisation on n-alkanes in isomerisation units, therefore, its cold filter plugging point (CFPP) may vary as desired from -5 to -40 °C [17,18]. The content of the isoalkanes greatly exceeds the content of the n-alkanes in the HVO with a low CFPP value [18].

HVO is fully miscible with conventional fossil diesel, but the low density of HVO is the main limitation to blend a high amount of HVO with diesel. However, HVO improves the cetane number of the blended diesel fuel linearly depending on the amount added [17].

In addition to diesel fuel, small amounts of bio-propane and light bio-hydrocarbons boiling to 180 °C are formed as side products. The light fraction (naphtha) can be blended into the gasoline where it provides a bio-component. Bio-propane can be used as a bio-component in LPG production or as a renewable source of processing energy in the HVO production to reduce the carbon footprint of the product. There is also the potential to produce Hydrotreated Esters and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK) which is also called green jet fuel [4,5].

The advantage of hydrotreating neat triglycerides is the possibility of optimising the reaction conditions, catalyst and unit construction depending on the composition of this specific raw renewable material. Also, the triglyceride feedstock can be upgraded in the existing refinery hydrotreating unit with some minor upgrades in its co-processing with petroleum middle distillate blends. However, it should be considered that vegetable oils contain trace inorganic contaminants like phosphorus, sodium, potassium and calcium, which can add deposits on the catalyst and cause its deactivation. Thus, a guard reactor may additionally be required to remove these contaminants [19]. The hydrotreating of triglycerides is quite exothermic and may require quenching capabilities that are not necessarily available in the existing reactor. The obtained by-products (H_2O, CO, CO_2) require a revision of the recycled gas system to remove them or the usage of a suitable gas cleaning process [19].

The hydrotreating of vegetable oils and animal fats is commonly carried out at a temperature range of 300-370 °C, at a pressure range of 2–10 MPa and in the presence of a suitable catalyst. Sulfided Ni-Mo, Co-Mo, noble metal (especially Pt or Pd) or reduced nickel catalysts are often used for this purpose. Al_2O_3, SiO_2, TiO_2, activated carbon or zeolites are usually used as supports in the catalysts [20-22].

Metal sulfided catalysts like Ni-Mo, Co-Mo, and Ni-W supported on alumina belong to the most important catalysts applied in the petroleum industry as they are used in hydrotreating and hydrocracking units to remove sulfur and nitrogen from petroleum fractions. The presence of sulfur in the feedstock is necessary to retain the activity of the catalysts for a long time. These types of catalysts are also commonly used for the hydrotreating of triglyceride-based materials in a neat form. Sulfur is found in very low concentrations in typical triglyceride-based materials [14], therefore, the addition of a suitable sulfur compound such as dimethyl disulfide [23] is necessary. The co-hydrotreating of triglycerides and petroleum feedstock does not require additional sulfur compounds due to the sulfur contained in the petroleum feedstock.

The hydrotreating reactor usually operates in the mixed-phase regime with a partially vaporised feedstock. The sulfur compounds contained in the feedstock are distributed between the liquid and vapour phases in accordance to their volatilities [24]. Therefore, the reaction rate of the hydrodesulfurisation is different in the gaseous and liquid phases. For example, in the case of hydrotreating middle distillates, a part of the feedstock is in a gas phase and the concentration of the hardly degradable and high boiling 4,6-dimethyl dibenzothiophene and other alkylated dibenzothiophenes in a liquid phase increases.

The hydrogen to feedstock ratio can change the conversion rate of the compounds with heteroatoms. The ratio must be kept high enough to maintain the desired hydrogen partial pressure in the hydrotreating reactor and to minimise the inhibiting effect of the hydrogen sulfide to the catalyst activity. The partial pressure of the hydrogen increases and the inhibiting effect of the hydrogen sulfide decreases in the hydrotreating reactor when the hydrogen to feedstock ratio increases [24]. The used hydrogen to feedstock ratio is often three or four times higher than the expected hydrogen consumption to ensure an adequate hydrogen supply through the reactor [24]. The hydrogen consumption depends on the composition of the feedstock, in particular on the sulfur, nitrogen and polyaromatic contents and is influenced by the type of catalyst used. For example, the use of a Ni-Mo catalyst results in the greater hydrogenation of the aromatics, therefore, the consumption of hydrogen is higher, when compared to a Co-Mo catalyst [25].

The presence of triglycerides in the feedstock has a strong influence on the hydrogen consumption. It depends on the structure (mainly the number of double bonds) and the concentration of the triglycerides and the preferred routes of the deoxygenation of the fatty acids to alkanes (see Figure 1). The industrial importance of the HDCx route is considerable. The alkane yield is slightly lower, but, at the same time, the consumption of hydrogen might be significantly reduced when compared to the HDCn and HDO routes. On the assumption that all the triglycerides will be converted by the HDCx route, 7 moles of hydrogen will be consumed (for rapeseed oil assuming four double bonds/mole) in comparison to the 10 and 16 moles of hydrogen consumed during the conversion of the same triglycerides via the HDCn and HDO routes, respectively (see Figure 1). However, if the total CO_2 produced by the HDCx would be converted to methane, 19 moles of hydrogen would be consumed in total (see Reaction 1-3).

The reaction conditions of hydrotreating the triglycerides can strongly affect the ratio of the deoxygenation routes. For example, with an increasing reaction temperature, the HDCx and HDCn reactions are promoted resulting in a small decrease in the liquid compound yield since the yield of the alkanes with an odd number of carbon atoms in the molecule grows at the expense of the ones with an even number. An increase of the isoalkane yield with the increasing temperature is advantageous because it could improve the low-temperature properties of the product [16]. On the other hand, a higher hydrogen pressure promotes the HDO reaction pathway [26].

In the case of the co-hydrotreating of the triglycerides and petroleum middle distillates, it is necessary, besides for the deoxygenation of the renewable part of the feedstock, to assure the deep desulfurisation of the petroleum components. Donnis et al. [13] showed that if a Ni-Mo/Al_2O_3 catalyst was used, the presence of rapeseed oil (RO) in the feedstock did not reduce the rate of desulfurisation of the gas oil. On the other hand, the conversion of monoaromatics to cycloalkanes was reduced by the presence of triglycerides in the feedstock, most likely due to the CO formed, which is known to be strongly adsorbed on the metal active sites of the catalyst [13].

The conversion of the polyaromatic compounds to monoaromatics was not influenced by the presence of RO in feedstock as aromatic hydrogenation proceeds quite fast under typical hydrotreating conditions. The aromatics contents are mainly determined by the thermodynamic equilibrium between the tri-, di- and monoaromatic compounds [13].

Templis et al. [27] found out that the rate of gas oil desulfurisation over a Co-Mo/Al_2O_3 catalyst decreased with an increasing palm oil content in the feedstock to 5 wt%, but did not change with its further increase to 10 wt%. On the other hand, Tomášek et al. [28] studied the hydrotreating of gas oil and rapeseed oil mixtures over a Co-Mo/Al_2O_3 catalyst and observed an increase in the sulfur content in products with an increasing RO content in the feedstock in the whole studied range of 0-20 wt%. The different behaviour of the Ni-Mo and Co-Mo catalysts was confirmed by Bezergianni et al. [29]. They found out that the hydrodesulfurisation effectiveness of the Ni-Mo catalyst is not affected by the addition of waste cooking oil (WCO) in contrast to the Co-Mo catalyst.

The hydrogen consumption for the transformation of the palm oil into HVO was estimated to be 210 $dm^3 \cdot kg^{-1}$ [27]. Similarly, Carmona et al. [30] reported a hydrogen consumption of 16-21 $g \cdot kg^{-1}$ of triglycerides, corresponding to 178-234 $dm^3 \cdot kg^{-1}$. These consumptions are given by way of example only, applies to a given feedstock, the catalysts used and the used reaction conditions. It varies depending on the reactions by which the feedstock is converted into hydrocarbons and the subsequent reactions, such as methanation and reverse water gas shift reactions.

Donnis et al. [13] compared the hydrotreating of light gas oil (S=1.27 wt%, N=170 mg·kg^{-1}, polyaromatics=12 wt%) and its mixtures with rapeseed oil (15 and 25 wt%) over a Ni-Mo/Al_2O_3 catalyst at the temperature of 350 °C, a pressure of 4.5 MPa and a liquid hourly space velocity (LHSV) of 1.5 h^{-1}. In the case of hydrotreating gas oil and an RO blend of 75:25 vol%, a higher (500 m^3·m^{-3}) hydrogen to oil ratio was used when compared to the other two tests (250 m^3·m^{-3}) to compensate for the higher hydrogen consumption in the RO conversion. The hydrogen consumption was 47 m^3·m^{-3} in the case of the pure gas oil and increased to 83 m^3·m^{-3} and 103 m^3·m^{-3} when feedstocks contained 15 and 25 wt% of RO, respectively.

In this work, the effect of the hydrogen to feedstock ratio on the composition and properties of the liquid products from the hydrotreating of the mixture of petroleum middle distillates and rapeseed oil in an 80:20 weight ratio was studied. The hydrotreating was carried out over a sulfided Ni-Mo/Al_2O_3 catalyst at the pressure of 4.0 MPa, a WHSV of 1.0 h^{-1}, and a temperature of 345 °C.

2. Experimental procedures

2.1. Materials

Straight run gas oil (SRGO) from crude oil distillation and light cycle oil (LCO) from fluid catalytic cracking in a weight ratio of 93:7 were used to mix the basic fossil component called “F0”. This mixture is commonly used in the Kralupy refinery (Unipetrol RPA) as a feedstock to produce winter diesel fuel. It was further mixed with rapeseed oil (RO) in the weight ratio of 80:20 to prepare the second type of feedstock called “F20”. The distribution of the acyl groups in the RO is presented in Table 1 and the basic properties of both feedstocks are summarised in Table 2. The commercial food RO contained 4 mg·kg^{-1} of sulfur and 8 mg·kg^{-1} of nitrogen. The C_{18} acyl groups represented more than 91 wt% of the total acyl groups contained in the RO.

2.2. Hydrotreating and products processing

The hydrotreating of both feedstocks was carried out in a tubular fixed-bed reactor with a co-current flow of feedstock and hydrogen. The hydrotreating reactor tube has dimensions of 658 mm in length and an internal diameter of 30 mm. The reactor tube was divided into three zones: an upper preheat zone, a catalyst bed zone, and a bottom zone. The catalytic bed zone was filled with 98 cm^3 (97 g) of commercial hydrotreating Ni-Mo/Al_2O_3 catalyst with a particle size reduced to the range of 0.25-0.42 mm. The catalyst was diluted with silicon carbide (particle size of 0.25-0.30 mm) in the volume ratio of 1:1. The catalyst was activated (sulfided) in situ. A simplified schematic diagram of the preheater and electrically heated reactor system and catalyst activation were described earlier [31].

Tab. 1 The distribution of the acyl groups in the RO (wt%)

Acyl group[a]	Content	Acyl group[a]	Content
C14:0	0.1	C18:1	60.0
C16:0	5.5	C18:2	20.3
C16:1	0.4	C18:3	8.8
C18:0	2.0	C20+	3.0

[a] The first number next to C is the number of the carbon atoms in the acyl group, the second number is the number of the double bonds in the hydrocarbon chain.

Tab. 2 The properties of the feedstocks used for the hydrotreating

Properties	F0	F20
Rapeseed oil (wt%)	0.0	20.0
Density at 15 °C (kg·m^{-3})	839	863
Viscosity at 40 °C (mm^2·s^{-1})	3.36	5.35
Sulphur (wt%)	0.30	0.24
Nitrogen (mg·kg^{-1})	154	125
Cetane index	53	-
Saturated hydrocarbons (wt%)	78.4	62.7
Monoaromatics (wt%)	11.4	9.1
Diaromatics (wt%)	8.9	7.1
Triaromatics (wt%)	1.3	1.0

For each reaction condition, ca. 300 cm^3 of the liquid product was collected into a measuring cylinder during the hydrotreating experiments. The liquid product was purged with hydrogen under a flow rate of 0.5 dm^3·min^{-1} at laboratory temperature for 2 h to remove the hydrogen sulphide and ammonia. The water in the liquid products formed by the HDO and HDCn reactions was then separated using a separating funnel.

All the liquid products were at first stabilised by removing the fraction boiling up to 150 °C in a Fischer HMS 500 distillation apparatus. The liquid products (ca 250 g) were first distilled at atmospheric pressure and then under a reduced pressure of 5 kPa until the temperature at the head of the column reached 64 °C, which is the boiling point corresponding to 150 °C under atmospheric pressure.

2.3. Analysis of the liquid products

The conversion of the rapeseed oil to hydrocarbons was verified by the simulated distillation of the liquid products using a TRACE GC ULTRA gas chromatograph according to the extended ASTM D2887 standard. The cetane index was calculated according to EN ISO 4264 using the density and the simulated distillation data converted to the ASTM D86 equivalent results.

The content of the sulfur and nitrogen in the liquid products was determined on a Trace Elemental Instruments Xplorer-NS according to the ASTM D5453 and ASTM D4629 procedures, respectively. The density was measured according to the EN ISO 12185 via an Anton

Paar DMA 4000 and the kinematic viscosity was measured according to the ASTM D7042 via an Anton Paar SVM 3000. The cold filter plugging point (CFPP) was measured according to the EN 116 on a Callisto 100 (Anton Paar) coupled to a Julabo FL 601 cryostat.

The n-alkane content in the liquid products was determined using an HP 6890 gas chromatograph equipped with a flame ionisation detector (GC-FID). The n-alkanes present were identified by comparing their retention times with those of a standard mixture of the C_6–C_{30} n-alkanes that was analysed under the same conditions as the samples. The content of each n-alkane was calculated as the relative ratio of the individual n-alkane area to the total product area. The conditions of the GC-FID analysis were provided in a previous article [32].

The group type composition of the stabilised liquid products was determined according to the EN 12916 procedure via high-performance liquid chromatography (HPLC) with refractometric detection and a normal phase arrangement.

2.4. Calculation of the hydrogen consumption

The mass flows of the individual components (sulfur, nitrogen, saturated compounds, monoaromatics, diaromatics, triaromatics, rapeseed oil (RO)) entering the reactor were calculated from the mass flow of the feedstocks and their composition according to Equation 1.

$$m_i^F = m^F \cdot w_i^F \qquad (1)$$

where m_i^F is the mass flows of the i component in the feedstock (g·h^{-1}), m^F is the mass flow of the feedstock (g·h^{-1}) and w_i^F is the mass fraction of the i component in the feedstock.

The mass flows of the individual components contained in the acquired stabilised liquid products were calculated according to Equation 2.

$$m_i^P = m^P \cdot w_i^P \qquad (2)$$

where m_i^P is the mass flow of i component contained in the stabilised liquid products (g·h^{-1}), m^P is the mass flow of the liquid product (g·h^{-1}) and w_i^P is the mass fraction of i component in the liquid product.

The hydrogen consumption for the hydrogenation of the double bonds in the rapeseed oil $m_{H_{DB}}$ in g·h^{-1} was calculated according to Equation 3.

$$m_{H_{DB}} = m_{RO}^{F20} \cdot A_{RO} \cdot \frac{M_{H_2}}{M_{RO}} \qquad (3)$$

where m_{RO}^{F20} is the mass flow of RO in the feedstock containing 20 wt% of RO (F20) in g·h^{-1}, A_{RO} is the average number of the double bonds in 1 mole of RO, M_{H_2} is the molar mass of the hydrogen and M_{RO} is the average molar mass of the RO, both in g·mol^{-1}.

The average number of the double bonds in the RO (A_{RO}) was calculated according to Equation 4.

$$A_{RO} = 3 \cdot (w_{Ac16}^1 + w_{Ac18}^1 + 2 \cdot w_{Ac18}^2 + 3 \cdot w_{Ac18}^3 + w_{Ac20}^1 + w_{Ac22}^1 + w_{Ac24}^1) \qquad (4)$$

where w_{Ac16}^1 is the mass fraction of the acyl with 16 carbon atoms and one double bond in the molecule (C16:1 acyl) relative to all the RO acyls. Similarly, w_{Ac18}^1, w_{Ac18}^2, w_{Ac18}^3, w_{Ac20}^1, w_{A22}^1 and w_{Ac24}^1 are the mass fractions of the C18:1, C18:2, C18:3, C20:1, C22:1 and C24:1 acyls.

The average molar mass of the rapeseed oil (M_{RO}) was calculated according to Equation 5.

$$M_{RO} = 3 \cdot M_C + 5 \cdot M_H + 3 \cdot \sum (w_{Aci} \cdot (C_i \cdot M_C + H_i \cdot M_H + 2 \cdot M_O)) \qquad (5)$$

where C_i and H_i are the numbers of carbon and hydrogen atoms in the *i* acyl, respectively, w_{Aci} is the mass fraction of the *i* acyl, M_C, M_H and M_O are the molar masses of the carbon, hydrogen and oxygen atoms in g·mol^{-1}, respectively.

The mass flow of the n-alkanes arising from the RO hydrotreating was calculated according to Equation 6.

$$m_{A_i}^{RO} = m_{A_i}^{P20} - (1 - w_{RO}^F) \cdot m_{A_i}^{P0} \qquad (6)$$

where $m_{A_i}^{RO}$ is the mass flow of the *i* n-alkane that originated from the RO, $m_{A_i}^{P20}$ is the mass flow of the *i* n-alkane in the product from the hydrotreating of the F20 feedstock, w_{RO}^F is the mass flow of RO in feedstock and $m_{A_i}^{P0}$ is the mass flow of the *i* n-alkane in the product from the hydrotreating of the neat petroleum feedstock (F0).

The C_{18} acyls, which form the major part of the RO acyls, provide the C_{18} n-alkane at the HDO reaction and the C_{17} n-alkane at the HDCx and HDCn reactions. The share of the HDO reaction in the RO conversion (A_{HDO}) was, therefore, calculated according to Equation 7.

$$A_{HDO} = \frac{n_{A_{18}}^{RO}}{(n_{A_{18}}^{RO} + n_{A_{17}}^{RO})} = \frac{\frac{m_{A_{18}}^{RO}}{M_{A_{18}}}}{(\frac{m_{A_{18}}^{RO}}{M_{A_{18}}} + \frac{m_{A_{17}}^{RO}}{M_{A_{17}}})} \qquad (7)$$

where $n_{A_{18}}^{RO}$ and $n_{A_{17}}^{RO}$ are the molar flows of the C_{18} and C_{17} n-alkanes arising from the RO hydrotreating in mol·h^{-1}, respectively, $m_{A_{18}}^{RO}$ and $m_{A_{17}}^{RO}$ are the mass flows of the C_{18} and C_{17} n-alkanes arising from the RO hydrotreating in g·h^{-1}, respectively, $M_{A_{18}}$ and $M_{A_{17}}$ are the molar masses of the C_{18} n-alkane and C_{17} n-alkane in g·mol^{-1}, respectively. It was assumed that the C_{14}, C_{16}, C_{20}, C_{22}, and C_{24} acyls contained in the RO were converted into odd-numbered alkanes and even-numbered alkanes in the same ratio as the C_{18} acyls.

The hydrogen consumption for the RO hydrodeoxygenation ($m_{H_{HDO}}$) in g·h^{-1} was calculated according to Equation 8.

$$m_{H_{HDO}} = m_{RO}^{F20} \cdot A_{HDO} \cdot \frac{12 \cdot M_{H_2}}{M_{RO}} \qquad (8)$$

The hydrogen consumption for the RO hydrodecarboxylation ($m_{H_{HDCx}}$) in g·h^{-1} was calculated according to Equation 9.

$$m_{H_{HDCx}} = m_{RO}^{F20} \cdot A_{HDCx} \cdot \frac{3 \cdot M_{H_2}}{M_{RO}} \qquad (9)$$

where A_{HDCx} is the relative range of the RO hydrodecarboxylation calculated from the molar flows of the C_{18} and C_{17} n-alkanes resulting from the conversion of the RO ($n_{A_{18}}^{RO}$ and $n_{A_{17}}^{RO}$, respectively) and the CO (x_{CO}) and CO_2 (x_{CO_2}) content in the gaseous products in mol% according to Equation 10.

$$A_{HDCx} = \frac{n_{A_{17}}^{RO}}{n_{A_{17}}^{RO} + n_{A_{18}}^{RO}} \cdot \frac{x_{CO_2}}{x_{CO_2} + x_{CO}} = (1 - A_{HDO}) \cdot \frac{x_{CO_2}}{x_{CO_2} + x_{CO}} \quad (10)$$

The CO and CO_2 contents in the gaseous products (1.5 and 3.6 mol%, respectively) were taken from a previous work [31] in which a similar hydrotreating of a feedstock containing 20 wt% of RO using a Ni-Mo/Al_2O_3 catalyst was executed (WHSV of 1.0 h^{-1}, 4.0 MPa pressure, temperature of 350 °C, hydrogen to feedstock ratio of 240 $m^3 \cdot m^{-3}$). It was assumed that the ratio of the CO and CO_2 contents in the gaseous products did not change as the hydrogen to feedstock ratio changed, although their concentrations increased significantly with a decreasing hydrogen to feedstock ratio.

The hydrogen consumption for the RO hydrodecarbonylation ($m_{H_{HDCn}}$) in $g \cdot h^{-1}$ was calculated according to Equation 11.

$$m_{H_{HDCn}} = m_{RO}^{F20} \cdot A_{HDCn} \cdot \frac{6 \cdot M_{H_2}}{M_{RO}} \quad (11)$$

where A_{HDCn} is the relative range of the RO hydrodecarbonylation.

At the full conversion of the RO to hydrocarbons, Equation 12 can be used for the A_{HDCn} calculation.

$$A_{HDCn} = (1 - A_{HDO} - A_{HDCx}) \quad (12)$$

The hydrogen consumption for the hydrodesulfurisation (HDS) of the feedstock ($m_{H_{HDS}}$) in $g \cdot h^{-1}$ was calculated according to Equation 13.

$$m_{H_{HDS}} = (m_S^F - m_S^P) \cdot \frac{2 \cdot M_{H_2}}{M_S} \quad (13)$$

where m_S^F and m_S^P are the mass flow of the sulfur in the feedstock and appropriate product in $g \cdot h^{-1}$, respectively, and M_S is the molar mass of sulfur in $g \cdot mol^{-1}$.

The calculation was performed assuming that 2 moles of hydrogen are consumed on average per 1 mole of sulfur in the feedstock. This is true for the direct HDS of alkyl sulfides, aryl sulfides, alkyl thiophenes, alkyl benzothiophenes and alkyl dibenzothiophenes. This assumption is not applicable to disulfides and thiols for which 3 and 1 moles of hydrogen are needed for their HDS, respectively. The hydrogen consumption for the hydrogenation of the unsaturated bonds resulting from the direct HDS and eventual hydrogenation of the aromatic rings, which occurs during the indirect HDS of the alkyl thiophenes, alkyl benzothiophenes and alkyl dibenzothiophenes, is reflected in the group composition changes. Therefore, it is not included in the hydrogen consumption for the HDS, but in the hydrogen consumption for the hydrodearomatisation ($m_{H_{HDA}}$) that is shown below.

The hydrogen consumption for the hydrodenitrogenation (HDN) of the feedstock ($m_{H_{HDN}}$) in $g \cdot h^{-1}$ was calculated according to Equation 14.

$$m_{H_{HDN}} = (m_N^F - m_N^P) \cdot \frac{2 \cdot M_{H_2}}{M_N} \quad (14)$$

where m_N^F and m_N^P are the mass flow of the nitrogen in feedstock and appropriate product, respectively, and M_N is the molar mass of the nitrogen atom in $g \cdot mol^{-1}$.

The calculation was performed assuming that of 2 moles of hydrogen are consumed on average per 1 mol of nitrogen in the feedstock. 2 moles of hydrogen are consumed for the HDN of the alkyl pyrroles, alkyl indoles and alkyl carbazoles, unless the hydrogenation of the double bonds in these compounds is considered. 1 moles of hydrogen is consumed for the HDN of the alkyl amines, 2.5 moles of hydrogen for the HDN of the alkyl pyridines, alkyl quinolines, alkyl benzoquinolines and alkyl acridines, unless the hydrogenation of the double bonds is taken into account. The hydrogen consumption for the hydrogenation of the unsaturated bonds of the nitrogen compounds and eventual hydrogenation of the aromatic rings, which occurs during the HDN of some nitrogen compounds, have an impact on the changes in the group composition, therefore, it was included in the hydrogen consumption for the hydrodearomatisation ($m_{H_{HDA}}$).

The calculation of the hydrogen consumption for the hydrodearomatisation (HDA) was performed using model compounds whose boiling points are in the range of 300-330 °C, which corresponds to the mean boiling point of the F0 feedstock (315 °C). The hydrogen consumption for the HDA of the feedstock ($m_{H_{HDA}}$) in $g \cdot h^{-1}$ was calculated according to Equation 15.

$$m_{H_{HDA}} = m_{H_{HDA}}^{TA} + m_{H_{HDA}}^{DA} + m_{H_{HDA}}^{MA} \quad (15)$$

where $m_{H_{HDA}}^{TA}$, $m_{H_{HDA}}^{DA}$, and $m_{H_{HDA}}^{MA}$ are the hydrogen consumptions to convert the triaromatics to diaromatics, diaromatics to monoaromatics, and the monoaromatics to saturated compounds, respectively.

The hydrogen consumption for the conversion of the triaromatics to diaromatics was calculated according to Equation 16.

$$m_{H_{HDA}}^{TA} = (m_{TA}^F - m_{TA}^P) \cdot \frac{2 \cdot M_{H_2}}{M_{TA}^{ST}} \quad (16)$$

where M_{TA}^{ST} is the molar mass of phenanthrene (m_{TA}^{ST}=178 $g \cdot mol^{-1}$) which was chosen as the triaromatic standard for the calculation, m_{TA}^F and m_{TA}^P are the mass flows of the triaromatics in the feedstock and the corresponding stabilised products in $g \cdot h^{-1}$, respectively.

The amount of triaromatics removed by the HDA m_{TA}^{Re} is approximately equal to the amount of diaromatics formed from them in $g \cdot h^{-1}$ (m_{DA}^{TA}) (Equation 17), which have to be taken into account when calculating the hydrogen consumption to convert the diaromatics into monoaromatics, which was, therefore, calculated according to Equation 18.

$$m_{DA}^{TA} \cong m_{TA}^{Re} = (m_{TA}^F - m_{TA}^P) \quad (17)$$

$$m_{H_{HDA}}^{DA} = (m_{DA}^F + m_{DA}^{TA} - m_{DA}^P) \cdot \frac{2 \cdot M_{H_2}}{M_{DA}^{ST}} \quad (18)$$

where M_{DA}^{ST} is the molar mass of the hexyl naphthalene (m_{DA}^{ST}=212 $g \cdot mol^{-1}$) which was chosen as the diaromatic standard for the calculation, m_{DA}^F and m_{DA}^P are mass flows of the diaromatics in the feedstock and the corresponding stabilised products in g·h^{-1}, respectively.

The monoaromatics amount formed by the hydrogenation of the diaromatics (m_{MA}^{DA}) is approximately equal to the amount of diaromatics removed during the hydrotreating (m_{DA}^{Re}) in g·h^{-1} (Equation 19), which have to be taken into account when calculating the hydrogen consumption needed to convert part of the monoaromatics into saturated hydrocarbons. It was calculated according to Equation 20.

$$m_{MA}^{DA} \cong m_{DA}^{Re} = (m_{DA}^{F} + m_{DA}^{TA} - m_{DA}^{P}) \qquad (19)$$

$$m_{H_{HDA}}^{MA} = (m_{MA}^{F} + m_{MA}^{DA} - m_{MA}^{P}) \cdot \frac{3 \cdot M_{H_2}}{M_{MA}^{ST}} \qquad (20)$$

where M_{MA}^{ST} is the molar mass of C_{12} alkyl benzene (m_{MA}^{ST}=246 g·mol^{-1}) which was chosen as the monoaromatic standard for the calculation, m_{MA}^{F} and m_{MA}^{P} are the mass flows of the monoaromatics in the feedstock and the corresponding stabilised products in g·h^{-1}, respectively.

The hydrogen consumption for the hydrotreating of the RO ($m_{H_{RO}}$) and the petroleum part of the feedstock ($m_{H_{PF}}$) was calculated according to Equations 21 and 22, respectively.

$$m_{H_{RO}} = m_{H_{DB}} + m_{H_{HDO}} + m_{H_{HDCx}} + m_{H_{HDCn}} \qquad (21)$$

$$m_{H_{PF}} = m_{H_{HDS}} + m_{H_{HDN}} + m_{H_{HDA}}^{TA} + m_{H_{HDA}}^{DA} + m_{H_{HDA}}^{MA} \qquad (22)$$

The total hydrogen consumption for the hydrotreating of the whole feedstock was calculated according to Equation 23. The feedstock cracking and methanation reaction were small [31], thus, the consumption of the hydrogen for these reactions was neglected.

$$m_{H_T} = m_{H_{PF}} + m_{H_{RO}} \qquad (23)$$

The excess hydrogen relative to its chemical consumption (Ex_H) was calculated according to Equation 24.

$$Ex_H = (m_H^F - m_{H_T})/m_{H_T} \qquad (24)$$

where m_H^F is the hydrogen mass flow used for the hydrotreating in g·h^{-1}.

The total volume of hydrogen consumption V_{H_T} in m^3·m^{-3} of feedstock was calculated according to Equation 25.

$$V_{H_T} = m_{H_T} \cdot V_{m_H}/(M_{H_2} \cdot V^F) \qquad (25)$$

where V_{m_H} is the hydrogen molar volume at 20 °C in dm^3·mol^{-1}, M_{H_2} is the hydrogen (H_2) molar mass and V^F is the feedstock volume flow in cm^3·h^{-1}.

3. Results and discussion

3.1. Product yield and labelling

The F0 feedstock was hydrotreated at the pressure of 4.0 MPa, a WHSV of 1.0 h^{-1}, a temperature of 345 °C and a hydrogen to feedstock ratio of 240 m^3·m^{-3}. These reaction conditions were selected so that the liquid product of the hydrotreating F0 feedstock contained ca 10 mg·kg^{-1} of sulfur. The F20 feedstock containing 20 wt% of the RO was hydrotreated at the same reaction temperature, pressure and WHSV, but under a variable hydrogen to feedstock ratio: 120; 240; 360; 480 and 600 m^3·m^{-3}. The labelling of the obtained liquid products and their yields are summarised in Table 3.

Tab. 3 Labelling and yields of the liquid products obtained

Feedstock	H_2/feedstock ratio (m^3·m^{-3})	Product label	Yield* (wt%)
F0	240	P0-240	98.0
F20	120	P20-120	94.8
F20	240	P20-240	95.6
F20	360	P20-360	94.2
F20	480	P20-480	93.4
F20	600	P20-600	94.1

* Related to the injection of the liquid feedstock

As was expected, the F20 feedstock provided less liquid product compared to the F0 one, since the HDO and HDCx/HDCn reactions of the RO produce more gaseous compounds as by-products, especially propane, CO_2 and CO. The yields of the stabilisation (distillation) of the obtained liquid products are shown in Table 4. The yields of the distillate and the distillation residue did not depend on the hydrogen to feedstock ratio.

Tab. 4 The mass balance of the liquid product stabilisation (wt%)

Product	Distillation residue	Distillate	Losses
P0-240	98.7	0.98	0.32
P20-120	98.5	1.15	0.40
P20-240	98.9	0.92	0.15
P20-360	98.8	1.19	0.14
P20-480	98.8	1.09	0.10
P20-600	99.0	0.96	0.06

3.2. Composition and properties of the stabilised liquid products

The simulated distillation results of all the liquid products showed the absence of substances boiling in the range of 400 to 550 °C, confirming that the conversion of the rapeseed oil was complete. The total RO conversion under these conditions is not surprising since triglycerides can be fully converted over a Ni-Mo/Al_2O_3 catalyst already at the temperature of 310 °C [16].

The properties and composition of stabilised hydrotreating products of both raw materials are summarised in Table 5. In the case of the F0 feedstock, the sulfur content decreased from 0.30 wt% to 10 mg·kg^{-1} in the P0-240 product. The nitrogen content was reduced from 154 mg·kg^{-1} to less than 2 mg·kg^{-1}. The decrease of the content of the diaromatics and triaromatics, which were converted mainly into monoaromatics was observed.

Tab. 5. The composition and properties of the hydrotreating products

Product	P0-240	P20-120	P20-240	P20-360	P20-480	P20-600
Density at 15 °C (kg·m^{-3})	840	833	832	829	829	829
Viscosity at 40 °C (mm^{2}·s^{-1})	3.46	3.48	3.45	3.46	3.45	3.45
Sulphur (mg·kg^{-1})	10	37	7	3	3	3
Nitrogen (mg·kg^{-1})	<2	8.3	<2	<2	<2	<2
Cetane index	53	58	59	60	60	60
CFPP (°C)	-7	-8	-9	-7	-7	-8
Saturated hydrocarbons (wt%)	79.9	81.4	82.5	83.6	84.3	84.3
Monoaromatics (wt%)	17.5	14.2	14.8	14.1	13.7	13.8
Diaromatics (wt%)	2.4	4.0	2.5	2.1	1.8	1.7
Triaromatics (wt%)	0.2	0.4	0.2	0.2	0.2	0.1

The content of the monoaromatics, thus, increased from 11.4 to 17.5 wt%, the saturated hydrocarbons content only increased by 1.5 wt%.

It is obvious that the hydrogen to feedstock ratio of 120 m^{3}·m^{-3} was not enough to desulfurise the F20 feedstock to a level of 10 mg·kg^{-1}, the value necessary to meet the EN 590 diesel fuel standard. The sulfur content in the products from the F20 feedstock hydrotreating decreased with an increasing hydrogen to feedstock ratio up to 360 m^{3}·m^{-3}, a further increase had no effect. A similar exponential decrease in the sulfur content, as a function of the increasing hydrogen to feedstock ratio, was reported by Hoekstra [24].

It can be seen from Table 5 that all the products from the processing of the F20 feedstock had a higher saturated hydrocarbon content and a lower aromatic content compared to the product obtained by the F0 feedstock hydrotreating. This is because the hydrotreating of the RO mainly produces alkanes. The saturated hydrocarbons content increased slightly with an increasing hydrogen to feedstock ratio up to 480 m^{3}·m^{-3}. The higher content of the saturated hydrocarbons caused an increase in the cetane index and a decrease in the density due to the chemical and physical properties of the alkanes when compared to the aromatics. The linear alkanes originating from the RO did not practically affect the CFPP of the products obtained. All the products of the hydrotreating met with the content of the polyaromatic hydrocarbons the EN 590 standard requirements for diesel fuel.

Tab. 6 The content of the n-alkanes in the liquid products (wt%)

Alkanes	P0-240	P20-120	P20-240	P20-360	P20-480	P20-600
n-C_{14-}	2.7	4.7	4.5	4.4	4.6	4.6
n-C_{15}	1.4	2.5	2.4	2.5	2.4	2.4
n-C_{16}	1.7	1.8	1.8	2.1	1.9	1.8
n-C_{17}	2.1	11.5	10.9	10.5	10.3	10.4
n-C_{18}	2.0	4.9	5.9	6.0	6.1	6.5
n-C_{19+}	4.8	4.3	4.3	4.4	4.3	4.3
Total	14.7	29.7	29.8	29.8	29.6	30.0

The total mass flow of the n-alkanes arising from the RO hydrotreating in the products (see Table 7) was 15.9-16.8 g·h^{-1}, which corresponds to their theoretical amount (16.5 g·h^{-1}) calculated from the RO composition assuming that 33 % of the RO was converted by the HDO reaction and the rest by the HDCx and HDCn reactions. This suggests that the isomerization of the n-alkanes was very low.

The content of the individual n-alkanes in all the liquid products is shown in Table 6. The P0-240 product prepared from the F0 feedstock did not contain high amounts of C_{17} and C_{18} n-alkanes in contrast to the P20 products. They contained higher amounts of C_{17} and C_{18} n-alkanes arising from the RO acyls. The content of the n-alkanes in the P20 liquid products did not change significantly with a change in the hydrogen to feedstock ratio. The content of the other n-alkanes was significantly lower since the C_{18} acyls represented more than 91 wt% of the acyl groups in the rapeseed oil (see Table 1).

It can be stated that 25-36 wt% of the RO was converted by the HDO route (Table 8) and the rest by the HDCn and HDCx routes. The proportion of the HDO reaction on the RO conversion increased slightly with an increasing hydrogen to feedstock ratio. A similar proportion of the HDO reaction in the triglyceride conversion (36 %) over a Ni-Mo/Al_2O_3 catalyst was reported by Carmona et al. [30].

Tab. 7 The mass flow of the n-alkanes arising from the RO hydrotreating in the liquid products (g·h^{-1})

Alkanes	P20-120	P20-240	P20-360	P20-480	P20-600
n-C_{14-}	2.3	2.2	2.0	2.2	2.2
n-C_{15}	1.3	1.2	1.2	1.1	1.2
n-C_{16}	0.4	0.4	0.6	0.4	0.4
n-C_{17}	9.1	8.7	8.1	7.9	8.1
n-C_{18}	3.0	4.0	4.0	4.1	4.5
n-C_{19+}	0.3	0.4	0.4	0.3	0.3
Total	16.4	16.8	16.3	15.9	16.6

Tab. 8 The share of the HDO, HDCx and HDCn reactions in the RO conversion

Alkanes	P20-120	P20-240	P20-360	P20-480	P20-600
A_{HDO}	0.24	0.30	0.32	0.33	0.35
A_{HDCx}	0.53	0.49	0.48	0.47	0.46
A_{HDCn}	0.23	0.21	0.20	0.20	0.20

Table 9 shows the chemical consumption of the hydrogen calculated as described in the experimental part of this work and the resulting hydrogen excess relative to its chemical consumption used in the hydrotreating experiments. It is apparent from these data that the addition of 20 wt% RO to the feedstock significantly increased the hydrogen consumption. At a hydrogen to feedstock ratio of 120 $m^3 \cdot m^{-3}$, the excess hydrogen was only 1.0, which was not enough for the desulfurisation of the petroleum part of the F20 feedstock. The hydrogen consumption increased with an increasing hydrogen to feedstock ratio as the ratio of the HDO route in the RO conversion and the HDA of the fossil part of the feedstock increased. The hydrogen excess of 2.5 was sufficient to obtain a product satisfying the requirements of the EN 590 standard for diesel fuel.

Tab. 9. The consumption and excess of the hydrogen in the hydrotreating experiments

Product	P0-240	P20-120	P20-240	P20-360	P20-480	P20-600
Hydrogen consumption ($m^3 \cdot m^{-3}$)	26	61	69	74	76	77
Hydrogen excess	8.4	1.0	2.5	3.9	5.3	6.8

3.3. Application of the liquid products in the diesel fuel production

In the production of diesel fuel, about 20 wt% of the hydrotreated kerosene is usually added to the hydrotreated gas oil. Therefore, hydrotreated kerosene (HKE) was added to the P0-240 and P20-240 products in a content of 10; 15; 20, and 25 wt% (Table 10). A density of 805 $kg \cdot m^{-3}$, a viscosity of 1.42 $mm^2 \cdot s^{-1}$, a sulfur content of 1 $mg \cdot kg^{-1}$ and a cetane index of 43 was measured for the HKE. The addition of HKE had the same effect on both of the compared products. It resulted in a decrease in the viscosity and density as expected. The CFPP decreased only a little for both types of hydrotreating products.

Tab. 10. The composition and properties of the P0-240 and P20-240 products and their mixtures with HKE

Product/mixture	P0-240	P0-240/10	P0-240/15	P0-240/20	P0-240/25	P20-240	P20-240/10	P20-240/15	P20-240/20	P20-240/25
HKE content (wt%)	0	10	15	20	25	0	10	15	20	25
Viscosity ($mm^2 \cdot s^{-1}$)	3.46	3.12	2.88	2.77	2.64	3.45	3.15	2.91	2.79	2.68
Density ($kg \cdot m^{-3}$)	840	836	834	832	831	832	828	826	825	824
CFPP (°C)	-7	-6	-9	-9	-10	-9	-7	-11	-12	-12

4. Conclusion

Mixtures of petroleum middle distillates with vegetable oils, animal fats or other triglyceride-based material can be co-hydrotreated in existing gas oil hydrotreating units. Triglycerides are mainly converted to alkanes and the renewable diesel component with a high cetane number and lower density in comparison with conventional fossil diesel is produced.

The hydrogen to feedstock ratio must be high enough to maintain the desired hydrogen partial pressure in the hydrotreating reactor to minimise the inhibiting effect of the hydrogen sulfide and carbon oxides. The sulfur content in liquid products of hydrotreating of feedstock containing 20 wt% of rapeseed oil decreased and the saturated hydrocarbon content slightly increased with an increasing hydrogen to feedstock ratio up to 360 $m^3 \cdot m^{-3}$, a further increase in the hydrogen to feedstock ratio had no significant effect. The linear alkanes originating from the rapeseed oil did not affect the CFPP of the products obtained.

The hydrogen to feedstock ratio of 120 $m^3 \cdot m^{-3}$ was not enough to desulfurise the feedstock containing 20 wt% of rapeseed oil to the 10 $mg \cdot kg^{-1}$ level. On the other side, the improvement of the properties of the products obtained by increasing the hydrogen to feedstock ratio from 240 $m^3 \cdot m^{-3}$ to 360 $m^3 \cdot m^{-3}$ was insignificant.

Therefore, the hydrogen excess of 2.5 (the hydrogen to feedstock ratio of 240 $m^3 \cdot m^{-3}$ in this case) can be considered to be sufficient for the hydrotreating of the feedstock containing 20 wt% of rapeseed oil over a Ni-Mo/Al_2O_3 catalyst. The composition and properties of the resulting liquid product were in accordance with the EN 590 standard requirements for diesel fuel. Additionally, the blending of this liquid product with hydrotreated kerosene up to 25 wt% is also possible and the basic properties of the blend are still in accordance with EN 590 standard requirements for diesel fuel.

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