Renewable Hydrocarbon Production via Rapeseed Oil Hydrotreatment Over Palladium Catalysts

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Abstract. The effect of SiO₂-Al₂O₃ (Pd5%/SA), activated carbon (Pd5%/C) and Al₂O₃ (Pd5%/A) supported palladium (5%) catalysts on renewable hydrocarbon synthesis via rapeseed oil hydrotreatment was investigated. The hydrotreatment experiments were carried out in solvent free medium under initial H₂ pressure 100 bar and at 340 °C temperature for 120 min using catalyst amount 5%. Gas chromatography-mass spectrometry (GC/MS) analysis were used for estimation of hydrocarbon content in the obtained samples. Pd5%/SA catalyst provided complete conversion of rapeseed oil into marketable liquid renewable hydrocarbons without presence of oxygen containing substances under studied hydrotreatment conditions. Moreover, all tested Pd catalysts gave partial feedstock conversion into hydrocarbons even in long residence time. Overall liquid hydrocarbon yields were from 55.3% to 82.3%.

1. Introduction

Growing population and industrialization has increased the world’s demand for energy and fuels. As fossil energy resources are limited, development of alternative green energy products are with great importance. In parallel, the development of agriculture in many countries has shown rapid growth and produced amounts of vegetable oils have increased. For example, EU have produced ~3.6 billion kg of rapeseed oil (RO) in the last year [1]. These renewable raw materials can be used as feedstock for first (1G) and second (2G) generation biofuel production. 1G can be manufactured by transesterification and esterification of glycerides and fatty acids, which lead to product – biodiesel. Although, biodiesel is known as alternative to petroleum diesel, it has some drawbacks as poor cold-flow properties and oxidation stability. It is less energy dense than liquid fossil fuels due to oxygen in fatty acid ester molecule. Another green biofuel obtainable from the same vegetable oils with similar properties to fossil fuels is “green diesel” or “hydrotreated vegetable oil” (HVO). HVO technologies include various catalytic reactions, such as, hydrogenation, hydrocracking, hydrodecarboxylation, hydrodecarbonylation, and hydrodeoxygenation of vegetable oils or animal fats under hydrotreating conditions at high temperature and pressure. The hydrotreating pathways and selectivity to particular products – renewable hydrocarbons - mainly depend on operating conditions and catalyst type (active metal, support, and promoter) [2].

Green diesel attracted wide attention as renewable fuel for diesel vehicles as well as sustainable aviation fuel [3]. HVO capacity within EU reached 3.5 Million tons in 2020 and it is forecasted to grow to 11.3 Million tons by 2025 [4]. Such market grow is initiated by EU new climate and energy policies according to which 14% of the energy consumed in road and rail transport must be from...
renewable sources by 2030 [5]. Green diesel presents excellent fuel properties, including higher cetane number, higher heating value, and negligible oxygen content than biodiesel, therefore research devoted to parameter optimization of HVO technology, different biomass feedstock utilization, selective and active hydrotreating catalyst synthesis is one of top priorities for EU to boost renewable energy shares in the transport sector.

Ni, Ni-Mo, and noble metals supported on activated carbon, SiO$_2$, Al$_2$O$_3$, SiO$_2$-Al$_2$O$_3$ etc. are typical hydrotreating catalysts for HVO synthesis from fatty acids and their glycerides containing feedstocks. Ni catalysts are low cost and relatively easy to synthesize and recycle, however, they also easily deactivate, showing low reusability [6]. On the other hand, some of noble metal catalysts like Pd and Ru possess high catalytic activity under relatively mild operating conditions even at low metal loadings and catalyst amounts towards feedstock. Unlike Ru catalysts, Pd supported on SiO$_2$-Al$_2$O$_3$ has comparatively high impact on hydrocarbon production by hydrodeoxygenation. This lead to increased hydrocarbon yield which is an important aspect for industrial application [7].

Present work demonstrates the effect of commercial Pd (active metal loading 5%) catalysts with three different supports (activated carbon, Al$_2$O$_3$, SiO$_2$-Al$_2$O$_3$) on hydrocarbon production from RO under similar hydrotreating conditions to evaluate their potential for practical application in HVO production.

**Table 1.** The list of abbreviations used in the text.

| Abbreviation | Description |
|--------------|-------------|
| 1G           | first generation |
| 2G           | second generation |
| DG           | diglyceride |
| n-C15        | n-pentadecane |
| n-C16        | n-hexadecane |
| n-C17        | n-heptadecane |
| n-C18        | n-octadecane |
| n-C19        | n-nonadecane |
| n-C22        | docosane |
| FT-IR        | Fourier transform infrared spectroscopy |
| GC/MS        | Gas chromatography-mass spectrometry |
| GC/FID       | Gas chromatography- flame ionization detector |
| HVO          | hydrotreated vegetable oil |
| MG           | monoglyceride |
| RME          | rapeseed oil methyl ester |
| RO           | rapeseed oil |
| TG           | triglyceride |

**Table 2.** The main characteristics of rapeseed oil (RO).

| Characteristic                  | RO            |
|--------------------------------|---------------|
| Monoglycerides, wt.%           | 0.2           |
| Diglycerides, wt.%             | 0.6           |
| Triglycerides, wt.%            | 98.7          |
| Saponification value, mg KOH/g | 190.4         |
| Acid value, mg KOH/g           | 0.1           |
| Calorific value, MJ/kg (d.b)   | 39.37         |
| Water content, wt%             | 0.03          |
| N, S                           | <0.3*         |

*Method detection limit

**Fatty acid composition, wt.%**

| Fatty Acid           | wt.% |
|----------------------|------|
| Palmitic acid (C16:0)| 5.0  |
| Stearic acid (C18:0) | 1.5  |
| Oleic acid (C18:1)   | 63.6 |
| Linoleic acid (C18:2)| 20.8 |
| α-Linolenic acid (C18:3)| 7.5  |
| Other fatty acids    | 1.6  |

2. Materials and Methods

2.1. Materials

Supported palladium catalysts - Pd 5% on activated carbon powder, standard, reduced, nominally 50% water wet (Pd5%/C), Pd 5% on alumina, powder (Pd5%/A), and Pd 5% on silica-alumina, powder (Pd5%/SA) - were supplied from Alfa Aesar, Sigma-Aldrich, and Riogen, respectively. n-Pentadecane n-C15 (99%), n-hexadecane n-C16 (99%), n-heptadecane n-C17 (99%), n-octadecane n-C18 (99%), n-nonadecane n-C19 (99%) and docosane n-C22 (99%), toluene (99.8%), derivatization reagent N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), analytical standards tricaprin, 1,2,4-butanetriol, methyl heptadecanoate, methyl esters of palmitic, stearic, oleic, linoleic and α-linolenic acid for gas chromatography-mass spectrometry (GC/MS) and gas chromatography-flame ionization detector (GC/FID) analysis were purchased from Sigma-Aldrich.

The refined RO delivered from local food grade vegetable oil producer Iecavnieks&Co was used in experiments. The main characteristics of RO is given in Table 2.
2.2. Characterization of rapeseed oil (RO) and hydrocarbon samples

The RO was analysed by gas chromatography (GC) system 7890A (Agilent Technologies) equipped with two capillary columns, two flame ionization detectors (FID) and 7683B automatic liquid sampler. HP-INNOWax (30 m × 0.25 mm × 0.25 μm) column was utilized for determination of fatty acid composition according to a modified EN 14103 standard method: carrier gas H2 flow rate 5 ml/min; detector temperature 390 °C; temperature program – 200 °C (hold 25 min). GC-FID data of rapeseed oil methyl ester (RME) analysis (99.4 %, prepared from RO and methanol in the presence of alkaline catalyst) was used for estimation of fatty acid composition. It was assumed that RO have the same fatty acid composition as RME. Methyl heptadecanoate was used as internal standard. Fatty acid methyl ester peaks were identified by comparing retention times of particular standards. DB5-ht (15 m × 0.32 mm × 0.10 μm) column was used for determination of monoglyceride (MG), diglyceride (DG), and triglyceride (TG) content in RO according to a modified EN14105 standard method: carrier gas H2 flow rate 2 ml/min; detector temperature 390 °C; temperature program – 50 °C (hold 5 min) → 180 °C (15 °C/min) → 230 °C (7 °C/min) → 370 °C (10 °C/min, hold 5 min). Derivatization reagent MSTFA and two internal standards tricaprin, 1,2,4-butanetriol were used in GC analysis. Composition of hydrocarbon samples were determined by GC/MS analysis, using gas chromatograph GCMS-QP2010 Ultra (Shimadzu) equipped with RTX-XLB capillary column (60 m × 0.25 mm × 0.25 mm), a quadrupole mass selective analyzer and secondary electron multiplier detector. The flow rate of carrier gas (He) was 2.4 ml/min. The injector and ion source temperatures were 300 and 220 °C, respectively. Temperature program: 40 °C (hold 2 min) → 320 °C (10 °C/min, hold 10 min). Total program time was 40 min and split ratio 300:1. Injection volumes of the liquid samples for GC analysis were 1.0 μl. The hydrocarbons and other compounds were identified by comparing their mass spectra with the NIST08 database and retention times with reference compounds. n-Alkanes n-C15-C19 were quantified using docosane (n-C22) as internal standard in the toluene solutions. Calibration curves for each compound Cn were generated by plotting the ratio of peak areas A(Cm) against the concentration ratio (c(Cm)/c(C22)) of the calibration samples, where n=15-19. The unknown hydrocarbon n-C15-C19 concentration in the sample were determined from obtained calibration curves. Each experiment and analytical procedure was repeated twice and the maximum relative standard deviation of the method is 3.5%.

Fourier transform infrared (FT-IR) stretching vibration band (1750 - 1700 cm⁻¹) was used for detection of the unconverted carboxyl and carbonyl compounds in the hydrocarbon samples. FT-IR spectrometer PerkinElmer Spectrum 100 equipped with accessory 100T was used. Method detection limit for the presence of carboxyl and carbonyl compounds in hydrocarbon samples is 0.5% and 1%. Water content in RO was determined using METTLER TOLEDO DL39 Karl Fischer coulometer according to the standard method ISO 12937. Acid value was determined according to the EN 14104 standard method. Saponification value was determined according to the ISO 3657 standard method. Calorific value was determined by C 200 (IKA) oxygen-bomb calorimeter according to the standard method DIN 51900-3:2005.

Overall liquid hydrocarbon yields (Y_CHI) were calculated by equation (1).

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Y_{\text{CHI}} = \frac{m_p - C_{\text{CHI}}}{m_f}
\]  

where \(m_p\) is the mass of product and \(m_f\) is the mass of feedstock, \(C_{\text{CHI}}\) hydrocarbon content determined by GC.

2.3. Catalytic tests

Hydrotreating process was investigated utilizing initial H2 pressure of 100 bar, operating temperature of 340 °C, residence time 120 min, mixing speed of 300 rpm and 5% of catalyst amount. Each experiment was conducted using 40 g of RO mixed with catalyst in a batch type stainless steel autoclave-reactor (Parker Autoclave Engineers). The reactor was equipped with magnetically coupled mechanical mixer (6 blade agitator impeller) and Sentinel Series Controller. Filled and sealed autoclave-reactor was purged with H2 (flow rate 10 ml/s) for 15 min to fully eliminate air atmosphere from the pressure vessel. Then H2 pressure was increased to necessary initial value. Hydrotreating
process was terminated after 120 min by switching off the mixer and rapid cooling of pressure vessel with air fan was performed. The 95-97% of liquid hydrocarbons and other substances produced in the process was easily separated from reaction mixture by centrifugation at 3000 rpm for 3 min. The rest of products were extracted with acetone. The acetone was recovered by distillation using rotary evaporator. Then thin layer of the sample in petri dish was dried at 120 °C for 20 min to remove water produced in hydrotreating process. The hydrocarbon samples isolated from reaction mixture by both methods were collected and used for determination of liquid hydrocarbon yields.

3. Results and Discussion

3.1. The effect of catalysts on hydrocarbon yield and composition

Feedstock used in hydrotreatment experiments was rapeseed oil with fatty acid composition given in Table 2. RO contains mainly unsaturated free fatty acids TG of carbon chain length C18 (93.4%). The feedstock also contains moderate amount of unsaturated C16 (5%) and low amount of fatty acids with hydrocarbon chain length higher than C18 (up to 1.6%). Low amount of other glycerides, water and fatty acids in RO indicates to excellent quality of the rapeseed oil.

Theoretically only dominant linear saturated hydrocarbons with carbon chain length analogous to fatty acid composition of feedstock or by one carbon atom shorter can be produced by main oxygen removal reaction pathways: hydrodecarboxylation, hydrodecarbonylation, and hydrodeoxygenation.

All Pd catalysts used in this study are completely different by support and specific surface area. The specific surface area of particles is a function of porosity, pore size distribution, shape, and size [8], and it is directly related to catalyst performance. Pd5%/C supported on activated carbon has the largest specific surface area (980 m²/g) among other two tested catalysts. Activated carbons as catalyst supports typically are highly porous materials with large specific surface area 950-2000 m²/g [9]. Despite great textural properties Pd5%/C showed average performance in comparison to other two catalysts (Figures 1-3). The hydrocarbon yield over Pd5%/C reached 69.7% in 120 min of residence time. The catalyst mostly produces n-C17 (58.4%) and n-C18 (18.9%) from C18 fatty acid glycerides of RO. Obtained hydrocarbon sample also consist partially converted oxygen containing intermediates, such as, alcohols and carbonyl compounds detected by GC/MS and FT-IR. Partial
conversion of feedstock at relatively long residence time can be related with catalyst structure and metal dispersion. Catalysts prepared from activated carbon commonly have lower bulk powder densities than SiO$_2$, Al$_2$O$_3$, and SiO$_2$-Al$_2$O$_3$. Large active metal particles and/or increased distance between each other, especially at low Pd loadings like 5% might be the reasons related with reduced performance. Excessive Pd dispersion in low density of highly porous Pd5%/C catalyst support can restrict the accessibility of feedstock molecules and other compounds produced during hydrotreating process to active metal phase on catalyst surface hindering their fast conversion into renewable hydrocarbons. Reduced performance of Pd5%/C also can be contributed to significant presence of water (50% of catalyst mass recommended by supplier for storage) in catalyst. Twice amount of wet Pd5%/C catalyst was used for hydrotreating test because half of catalyst mass is water. Elevated amount of water in reaction mixture from catalyst can negatively affect reaction equilibrium, reaction rate, and overall conversion of feedstock into desired product – pure hydrocarbons without presence of oxygen containing compounds. The lowest yield (55.3%) of renewable hydrocarbons was obtained in the presence of Pd5%/A. The catalyst has almost ten times lower specific surface (101 m$^2$/g) area than Pd5%/C. This could be one of the main reasons for reduced performance to achieve high conversion of feedstock into pure renewable hydrocarbons in short residence time. The catalyst produces 51.2% of $n$-C17 and 9.2% of $n$-C18. The hydrocarbon sample similarly to that obtained over Pd5%/C also contains considerable amount of partially converted oxygen compounds (Figure 3).

The highest hydrocarbon yield (82.3%) was achieved over Pd5%/AS catalyst. The catalyst has large specific surface area 460 m$^2$/g. In the presence of Pd5%/SA catalyst under studied experimental conditions complete RO conversion into pure marketable hydrocarbons was accomplished. The hydrocarbon composition was $n$-C15 (2.5%) $n$-C16 (1.9%) $n$-C17 (56.3%) $n$-C18 (35.5%) and $n$-C19 (3.8%). All three catalysts produce low amount of $n$-C19 from C20 fatty acid glycerol esters, which is present in rapeseed oil in small quantities. Many factors can affect catalyst performance and selectivity to particular hydrocarbons in high temperature and pressure processes like HVO production. Active metal type, loading, dispersion, support type, textural properties, particle size, surface morphology, and composition are the key factors affecting catalytic performance.
factors related with catalyst structure. Experimental conditions are the second major factor which affects the product yield and composition. Tested catalysts exhibit different performance and selectivity in hydrocarbons synthesis from RO. The catalysts by performance can be arranged in following order - Pd5%/SA > Pd5%/C > Pd5%/A. Hydrodeoxygenation is most advantageous reaction pathway for hydrocarbon production. The maximum liquid hydrocarbon yield can be obtained only by hydrodeoxygenation. n-C17/n-C18 ratio show the effect of catalysts on hydrodeoxygenation. The n-C17/n-C18 ratios produced over Pd5%/SA, Pd5%/C, and Pd5%/A are 1.6, 3.1, and 5.6, respectively. The order of catalysts by selectivity to hydrocarbons produced by hydrodeoxygenation is analogous to their performance. According to literature data and our previous study [6] the selectivity is directly related with active metal type, support and its acidic sites. Evidently, the SiO2·Al2O3 and activated carbon of catalysts Pd5%/SA and Pd5%/C are supports with abundant acidic sites, which have pronounced impact on hydrodeoxygenation reaction. All tested Pd catalysts possess certain activity in HVO production from RO. However, the best results were achieved over Pd5%/SA due to high yield and full conversion of feedstock into desired product at relatively mild solvent-free one-pot operating conditions. Produced pure linear saturated renewable hydrocarbons with high calorific value 47.15 MJ/kg can be used in different areas similarly to those obtained from fossil sources.

4. Conclusions
Pd as active metal supported on three different carriers Al2O3 (Pd5%/A), SiO2·Al2O3 (Pd5%/SA), and activated carbon (Pd5%/C) showed sufficient activity in hydrocarbon synthesis from rapeseed oil. The catalysts by performance and selectivity to hydrocarbons produced by hydrodeoxygenation can be arranged in following order: Pd5%/SA > Pd5%/C > Pd5%/A. Only Pd5%/SA converted RO into pure marketable hydrocarbons with high calorific value 47.15 MJ/kg, yield (82.3%), and composition: n-C15 (2.5%), n-C16 (1.9%), n-C17 (56.3%), n-C18 (35.5%), and n-C19 (3.8%) without presence of oxygen containing compounds. Pd5%/C and Pd5%/A have significantly lower activity and impact on hydrodeoxygenation reaction. Depending on support type and catalyst characteristics Pd as active metal has potential for practical application in solvent-free one-pot renewable hydrocarbon synthesis from vegetable oils using relatively mild hydrotreating reaction conditions.

5. References
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