The Synthesis of Renewable Hydrocarbons from Vegetable Oil Feedstock in the Presence of Ni-supported Catalysts

Kristaps Malins
Riga Technical University, Institute of Applied Chemistry
Paula Valdena Str. 3, Riga, Latvia
mkrist@inbox.lv or kristaps.malins@rtu.lv

Abstract – The effects of commercial $Ni65\%/SiO_2-Al_2O_3$ and prepared $Ni10\%/SiO_2-Al_2O_3-135I$ Ni-supported catalysts and their amount (1.5-10%) on hydrocarbon production from rapeseed oil/it fatty acid (RO/RFA, weight ratio 1/1) feedstock were investigated. The textural properties of catalysts were characterized by N_2 sorption analysis and active metal loading by XRF. The activity of catalysts was evaluated by minimum oxygen removal reaction time determined from pressure-time profiles at studied operating temperature 340 ºC and initial H_2 pressure of 100 bar. GC analysis of obtained hydrocarbon mixtures was used for determination of dominant hydrocarbon *n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane composition. Both catalyst have proper activity for complete conversion of RO/RFA into marketable hydrocarbon mixture with high yield (76.1%-83.2%), calorific value (47.20-47.24 MJ/kg) and energy recovery (ER) (90.7%-99.1%) produced at residence time ~35-52 min. $Ni65\%/SiO_2-Al_2O_3$ has higher activity, but $Ni10\%/SiO_2-Al_2O_3-135I$ deliver elevated yield of hydrocarbons. Both catalysts with different selectivity have a potential for practical application in hydrotreated vegetable oil production processes.

Keywords: Nickel, Supported catalysts, Hydrocarbons, Hydrotreatment, Deoxygenation, Vegetable oil.

1. Introduction

Long hydrocarbon chains in fatty acid or their glyceride molecules extracted from biomass is perfect feedstock for renewable hydrocarbon production by hydroprocessing. Produced renewable paraffins is sometimes termed as second generation biofuel or hydrotreated vegetable oil or "green diesel" [1]. Unlike biodiesel (fatty acid alkyl esters) produced from triglycerides by alkali catalyzed transesterification reaction with lower alcohols, green diesel is more stable during storage, energy dense and compatible with common diesel engines. Furthermore, renewable hydrocarbons depending on their composition can be used not only as fuel for diesel engines, but also in various industrial areas similarly to hydrocarbons produced from fossil sources. Renewable hydrocarbons produced from vegetable oil or animal fat feedstock do not contain sulphur or aromatic compounds which is difficult to remove by specific and expensive treatment technologies, therefore are more favorable [2]. Production process of hydrotreated vegetable oil, which normally occur simultaneously, was first commercialized by the Neste Oil company (Finland). Following this progress, several other production units have been developed around the world. Hydrotreatment of vegetable or animal oils is catalytic process and can occur by general reaction pathways – hydrogenation, hydrocracking, hydrodeoxygenation, hydrodecarbonylation and hydrodecarboxylation. The hydrotreatment process can be performed in solvent free, water and hydrogen donor, such as, tetralin, decalin and isopropanol medium [3]. Typically, reaction kinetics and impact on the hydrotreating process have been investigated in the presence of some platinum group Pt, Pd, Rh, Ru and non-noble Ni, Mo, Co, Cu, Fe metals supported on SiO_2, Al_2O_3, ZrO_2, activated carbon or other materials [2, 4,5]. The metal supported catalysts can be prepared by several impregnation techniques [6]. The reaction pathways mainly depend on particular catalyst support, active metal, its loading and hydroprocessing conditions [5, 7, 8]. Hence, all those factors determine catalyst activity and selectivity. The noble metal catalysts have high performance in the vegetable or animal oil hydrodeoxygenation reactions, however, they are expensive and can be easily deactivated, which limit application in large scale production [4]. Non-noble catalysts are low cost, easy to obtain, recycle and suitable for different catalytic environments. Usually they require relatively high reaction pressure (5–15 MPa) and temperature (300–500 °C), but there are also many reports in the literature, when successful conversion of vegetable or animal oil feedstock was provided under more gentle conditions [6, 9].

Present study is devoted to investigation of vegetable oil feedstock conversion by hydrotreatment into renewable linear hydrocarbons over two different nickel-supported catalysts – commercial $Ni65\%/SiO_2-Al_2O_3$ and prepared $Ni10\%/SiO_2-Al_2O_3-135I$ using incipient wetness impregnation with following calcination and reduction. Rapeseed oil/it fatty acid (RO/RFA, weight ratio 1/1) mixture was utilized as model for hydrotreatment experiments to ensure reaction

environment similar to industrial, when low cost feedstock with high fatty acid content has been utilized for "green diesel" production.

2. Experimental
2.1. Materials

Ni(NO$_3$)$_2 \cdot$6H$_2$O (99%) was supplied from *Acros organics*. Ni65%/SiO$_2$-Al$_2$O$_3$ (powder) and catalyst support SiO$_2$–Al$_2$O$_3$ (grade 135), Ni powder (1 μ, 99.8%), derivatization reagent *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA), analytical standards tricaprin, 1,2,4-butanetriol, methyl heptadecanoate, methyl esters of stearic, palmitic, oleic, linoleic and α–linolenic acid, *n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane for GC analysis were purchased from *Sigma-Aldrich*. The refined RO delivered from local food grade vegetable oil producer *Iecavnieks & Co* was used in experiments. Rapeseed oil fatty acids (RFA) were prepared from RO. The main characteristics of RO and RFA are given in Table 1.

Table 1: The main characteristics of rapeseed oil (RO) and its fatty acids (RFA).

	RO	RFA
Monoglycerides, wt.%	0.2	0.4
Diglycerides,wt.%	0.5	-
Triglycerides, wt.%	98.5	-
Saponification value, mg KOH/g	190.0	N.A[a]
Acid value, mg KOH/g	0.23	197.3
Methyl esters, wt.%	-	-
Calorific value, MJ/kg (d.b)[b]	39.70	39.49
Water content, wt%	0.03	0.02
C/H	6.7	6.4
N, S		≤0.3[b]
Fatty acid composition, wt.%		
Palmitic acid (C16:0)		4.9
Stearic acid (C18:0)		1.1
Oleic acid (C18:1)		62.8
Linoleic acid (C18:2)		21.9
α–Linolenic acid (C18:3)		7.8
Other fatty acids		1.4

[a] Not analyzed.
[b] Method detection limit (MDL).

2.2. Preparation of rapeseed oil fatty acids

RFA were prepared from RO in complete saponification reaction with aqueous NaOH and following treatment with aqueous HCl. NaCl, HCl, glycerol and other impurities dissolved in water were removed from RFA using separatory funnel. RFA were washed several times with hot distilled water and then dried with rotary evaporator in vacuum (0.9-1.5 kPa) at 90–100 ºC for 30 min.

2.3. Preparation of catalysts

Commercial powdery SiO$_2$–Al$_2$O$_3$ (grade 135) was used as catalyst support. Before impregnation the catalyst support was calcined in air at 500 ºC for 6 h. The incipient wetness impregnation method was used for catalyst synthesis. Saturated Ni(NO$_3$)$_2 \cdot$6H$_2$O solution in distilled water was added drop by drop to the support for 1 h at 70 ºC temperature in closed 250 ml flask while intense stirring (350 rpm) with mechanical mixer. Then the mixture was stirred for additional 1 h at this temperature. Impregnated catalyst support was dried overnight at room temperature and then calcined in air at 500 ºC (4 ºC/min, hold 4 h).

Calcined catalysts were reduced in Parker Autoclave Engineers batch type stainless steel autoclave-reactor (designed to maximum pressure 343 MPa at 379 ºC, volume 500 ml) at temperature 320 ºC (5/min ºC) and initial H$_2$ pressure 70 bar for 3 h. Filled and sealed autoclave-reactor was properly purged with H$_2$ (flow rate 10 ml/s) for 15 min to fully eliminate the air atmosphere before reduction. After the reduction process H$_2$ flow (20 ml/s, 20 min) was utilized for removal of water vapors produced from catalyst.

2.4. Characterization of catalysts

N_2 sorption analysis was performed with a Quadrasorb SI surface area and pore size analyzer at −195.85 ºC (Quantachrome Instruments). The specific surface areas were determined using multipoint Brunauer–Emmett–Teller (BET) method based on the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. The total pore volumes were estimated from the amount of N_2 adsorbed at P/P_0 of 0.99. The maximum relative standard deviation (RSD) of method is 10%.

The active metal loading was determined by Supermini bench-top sequential wavelength dispersive X-ray fluorescence (XRF) spectrometer (Rigaku) in He atmosphere. Powdery mixtures of canalyst support SiO_2–Al_2O_3 (grade 135) and Ni powder (1 μ, 99.8%) were used as standards for calibration. The maximum RSD of method is 5%.

2.5. Characterization of rapeseed oil (RO), its fatty acids (RFA) and hydrocarbon samples

Model feedstock RO, RFA and obtained hydrocarbons in hydrotreating process were analyzed 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 H_2 flow rate 5 ml/min; detector temperature 390 ºC; temperature program – 200 ºC (hold 25 min). Rapeseed oil methyl ester (RME) sample (99.2%, prepared from RO and methanol in the presence of alkaline catalyst) was used for calculation of fatty acid composition. It was assumed that RO and RFA 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 and RFA according to a modified EN14105 standard method: carrier gas H_2 flow rate 2 ml/min; detector temperature 390 ºC; temperature program – 50 ºC (hold 5 min) → 180 ºC (15 ºC/min) → 230 ºC (7 ºC/min) → 370 (10 ºC/min, hold 5 min). Derivatization reagent MSTFA and two internal standards tricaprin, 1,2,4-butanetriol were used in GC analysis. The hydrocarbon contents in liquid samples obtained in hydrotreating process were determined in similar manner utilizing tricaprin as internal standard. Analytical standards *n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane were used for identification of specific hydrocarbon peaks in chromatogram.

Injection volumes of all samples for GC analysis were 1.0 µl. The maximum RSD of the methods is 2%.

Fourier transform infrared (FT-IR) stretching vibration band in the range of 1750 - 1700 cm^{-1} was used for detection of the unconverted carboxyl and carbonyl compounds in hydrocarbon mixture. FT-IR spectrometer PerkinElmer Spectrum 100 equipped with accessory 100T was utilized for analytical procedures. It was experimentally investigated that method detection limit (MDL) for the presence of carboxyl and carbonyl compounds in hydrocarbon mixture is 0.5% and 1%, respectively.

Water content in liquid samples 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 (HHV) was determined using C 200 (IKA) oxygen-bomb calorimeter according to the standard method DIN 51900-3:2005.

C, H, N, S elemental analysis was determined by EA3000 (EuroVector) elemental analyzer.

2.6. Catalytic tests

The effects of synthesized (Ni10%/SiO_2-Al_2O_3-135I) and commercial (Ni65%/SiO_2-Al_2O_3) catalysts on RO/RFA (weight ratio 1/1) conversion into renewable hydrocarbons by hydrotreating process were investigated utilizing initial H_2 pressure of 100 bar, operating temperature of 340 ºC, mixing speed of 300 rpm and different catalyst amount (1.5-10%).

Each experiment was conducted using 50 g of RO/RFA (weight ratio 1/1) mixed with catalyst in a batch type stainless steel autoclave-reactor (Parker Autoclave Engineers) used for catalyst reduction. 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 H_2 (flow rate 10 ml/s) for 15 min to fully eliminate air atmosphere from the pressure vessel. Then H_2 pressure was increased to necessary initial value.

Hydrogenation of –C=C– bond and general oxygen removal reactions (hydrodeoxygenation, hydrodecarboxylation and hydrodecarbonylation) of vegetable oil or fatty acids are complicated process and it consume H_2 in significant amount [1]. Oxygen removal step occurs at significantly higher temperature than hydrogenation and can be identified

by obvious change of pressure in pressure-time profiles of the hydrotreating process. Change of the pressure value from the maximum to minimum at operating temperature during hydrodeoxygenation, hydrodecarboxylation and hydrodecarbonylation step was used for estimation of minimum oxygen removal reaction time (Table 2). It is time when highest H_2 consumption was observed and largest part of RO/RFA converts into hydrocarbons and particular amount of their intermediates. Despite high repeatability of catalytic test results this parameter determined from pressure-time profiles is not absolute and serves for estimation of catalyst activity and overall residence time. After the minimum oxygen removal reaction time + additional 25 min the hydrotreating process was terminated by switching of the mixer and rapid cooling of pressure vessel with air fan. The 95%-97% of 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 by acetone. The acetone was recovered by distillation using rotary evaporator. After acetone recovery thin layer of the samples in Petri dish was dried at 120 ℃ for 20 min to remove water produced in hydrotreating process. The mixture of samples recovered by both methods was used for determination of hydrocarbon yields and other characterizations.

2.7. Calculations

Each experiment was repeated twice. Absolute experimental values were expressed as arithmetic mean from the two independently repeated experiments. A third independent experiment was performed in cases when previous two experimental values differed more than 5%. The average result of experiment with maximum RSD 3.0% was determined using two closest experimental values. The absolute values of all quantitative analysis data were obtained in similar manner.

Energy recovery (ER) calculated by Eq. (1) is an important parameter to evaluate the influence of experimental conditions on overall conversion of feedstock RO/RFA mixture into desired product – hydrocarbons.

$$\mathbf{ER}\ (\%) = \frac{\mathbf{CV_P \cdot Y_P}}{\mathbf{CV_F}} \tag{1}$$

where CV_P and CV_F are calorific values of product and feedstock, respectively. Y_P (%) is overall yield of products calculated by Eq. (2).

$$\mathbf{Y_P}\ (\%) = \frac{\mathbf{m_p}}{\mathbf{m_f}} \cdot \mathbf{100} \tag{2}$$

where m_P is the mass of product and m_F is the mass of feedstock.
Y_{CH} (%) (Eq. (3)) is the yield of the dominant hydrocarbons (*n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane) produced in the hydrotreating process.

$$\mathbf{Y_{CH}}\ (\%) = \frac{\mathbf{Y_P \cdot C_{CH}}}{\mathbf{100}} \tag{3}$$

where C_{CH} is *n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane content determined by GC.

3. Results and discussion
3.1. The effect of catalyst type and amount on hydrocarbon production from rapeseed oil and it fatty acid feedstock

The average molecular size of feedstock RO, RFA and partially converted intermediates in hydrotreating process are roughly ≤4 nm [10]. Both catalysts utilized for catalytic tests have high specific surface area, total pore volume and sufficient average pore diameter (Table 2). Commercial catalyst Ni65%/SiO$_2$-Al$_2$O$_3$ showed significantly higher activity than prepared Ni10%/SiO$_2$-Al$_2$O$_3$-135I. Catalytic performance depends on many characterizations of Ni-supported catalysts, but active metal loading is one of the key factors. Typically, enough high active metal loading ensures high activity of supported catalysts [5]. The minimum time necessary for main oxygen removal reactions (hydrodeoxygenation, hydrodecarboxylation and hydrodecarbonylation) is ~7 times shorter for Ni65%/SiO$_2$-Al$_2$O$_3$ in comparison to Ni10%/SiO$_2$-Al$_2$O$_3$-135I when identical catalyst amount (5%) was used in the process (Table 2). However, overall residence time of hydrocarbon production in the presence of catalyst with low active metal loading can be reduced with increase of catalyst amount.

Table 2: Textural properties, the effect of Ni-supported catalyst type and their amount on minimum oxygen removal reaction time of rapeseed oil and its fatty acid (RO/RFA, weight ratio 1/1) feedstock conversion into hydrocarbons by hydrotreatment.

	Ni^a, wt.%	S_{BET}^b, m^2/g	V^c, cm^3/g	D^d, nm	Minimum oxygen removal reaction time^e, min ($\pm3\%$)	Catalyst amount, %
Ni65%/SiO$_2$-Al$_2$O$_3$ *Commercial*	64.7	165	0.25	6.0	17.0 16.5 10.3	1.5 2.0 5.0
Ni10%/SiO$_2$-Al$_2$O$_3$-135I *Prepared*	9.4	412	0.51	5.0	74.2 26.8	5 10

^{a} Metal loading determined by XRF;
^{b} Specific surface area;
^{c} Total pore volume;
^{d} Average pore diameter;
^{e} Main reactions - hydrodeoxygenation, hydrodecarboxylation and hydrodecarbonylation; Determined from the pressure-time profiles of hydrotreating process.

The mass fraction of active metal Ni in reaction mixture is close for both catalysts when catalyst amount 10% of Ni10%/SiO$_2$-Al$_2$O$_3$-135I and 1.5% of Ni65%/SiO$_2$-Al$_2$O$_3$ are being utilized in process. Under these experimental conditions minimum oxygen removal reaction time over prepared catalyst was only by 9.8 min ($\pm3\%$) longer in comparison with Ni65%/SiO$_2$-Al$_2$O$_3$. This observation confirms, that mass fraction of active metal Ni provided by amount of supported catalyst in the reaction mixture have significant impact on reaction rate and conversion. Commercial catalyst Ni65%/SiO$_2$-Al$_2$O$_3$ ensures high RO/RFA conversion at short residence time using low catalyst amounts (Fig.1.). On the other hand, overall yield of all products including dominant hydrocarbons (*n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane) is higher for Ni10%/SiO$_2$-Al$_2$O$_3$-135I.
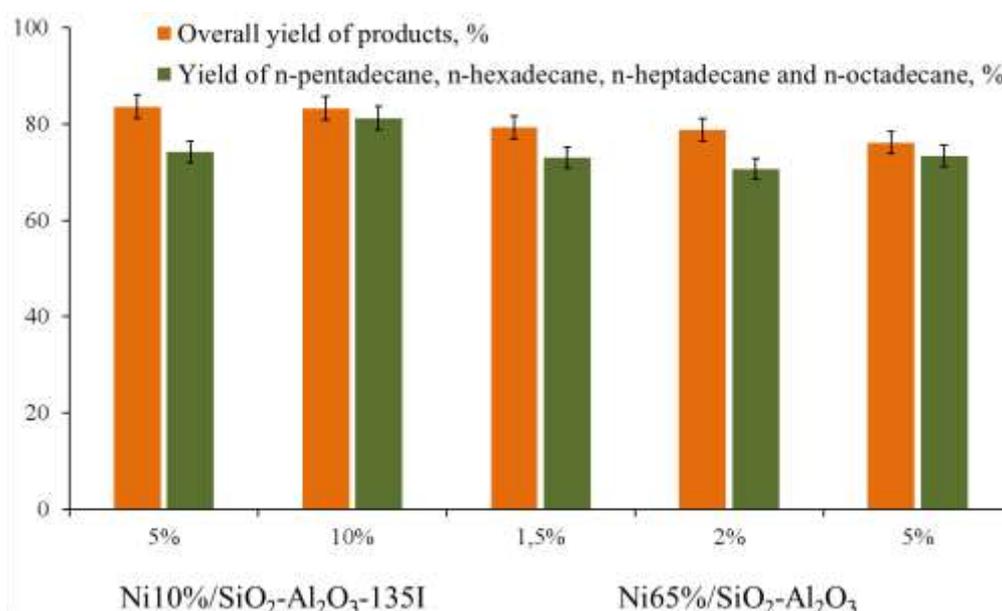

Fig. 1: The effect of catalyst type and amount on product yields. Hydrotreating conditions: operating temperature 340 °C, initial H$_2$ pressure 100 bar, mixing speed 300 rpm, overall residence time (minimum oxygen removal reaction time from Table 2 + 25 min).

Overall yield of products extracted from reaction mixture after hydrotreating process in the presence of Ni10%/SiO$_2$-Al$_2$O$_3$-135I and Ni65%/SiO$_2$-Al$_2$O$_3$ was in range of (83.2%-83.6%) and (76.1%-79.2%), respectively. Furthermore, highest yield of dominant hydrocarbons (73.4%-81.2%) was achieved utilizing maximum amount of studied catalysts. Highest overall yield of all products and four dominant hydrocarbons in mixture obtained in the presence of Ni10%/SiO$_2$-Al$_2$O$_3$-135I was ~7% and ~8% higher in comparison to Ni65%/SiO$_2$-Al$_2$O$_3$. Hence, energy

recovery also was ~9% higher and reached 99.1%. It can be explained that Ni10%/SiO$_2$-Al$_2$O$_3$-135I gave hydrocarbon mixture with high *n*-octadecane content (58.4%) produced in hydrodeoxygenation reactions (Fig. 2.). The mixture contains also *n*-heptadecane in large quantity and it was produced by other two oxygen removal pathways - hydrodecarboxylation and hydrodecarbonylation [1]. Catalytic transformation of feedstock containing mostly C$_{18}$ fatty acids (Table 1) into *n*-octadecane instead of *n*-heptadecane increases overall hydrocarbon yield and ER due to it has 5.8% higher molecular weight than later one. Opposite to prepared catalyst Ni65%/SiO$_2$-Al$_2$O$_3$ produces mostly *n*-heptadecane. The *n*-heptadecane content reached 82% using the highest catalyst amount. Furthermore, slightly elevated *n*-pentadecane and *n*-hexadecane content in the obtained hydrocarbon mixture was observed using commercial catalyst. Most rather decrease of overall yield in the presence of Ni65%/SiO$_2$-Al$_2$O$_3$ increases C$_{15}$-C$_{16}$ content. Seems that under studied experimental conditions Ni65%/SiO$_2$-Al$_2$O$_3$ promotes also slight cleavage of –C–C– hydrocarbon bond and produce aliphatic compounds with lower molecular weight than C$_{17}$-C$_{18}$. Some light hydrocarbons produced in the process might be lost during hydrocarbon extraction procedures. It reduces overall yield of products and ER. Marketable hydrocarbon mixtures without evidence of dissolved carboxyl and carbonyl compounds (FT-IR, detection limit less than 0.5-1.0%) were obtained using only maximum catalyst amounts. The mixtures have high calorific value (47.20-47.24 MJ/kg) and dominant hydrocarbon content (96.4-97.6%). The rest is hydrocarbons with wide range of molecular weight (analyzed by GC) produced from other fatty acids in oxygen removal reactions and by cleavage of –C–C– hydrocarbon bond. Other samples with similar calorific value contain particular amount of partially converted oxygen containing intermediates. Both catalysts have different selectivity and activity. Ni65%/SiO$_2$-Al$_2$O$_3$ has higher activity, but Ni10%/SiO$_2$-Al$_2$O$_3$-135I better selectivity to reach maximum overall yield of marketable product and ER. Investigated advantages of both catalysts are important for consideration of their utilization potential in hydrocarbon production from various fatty acid containing feedstock.
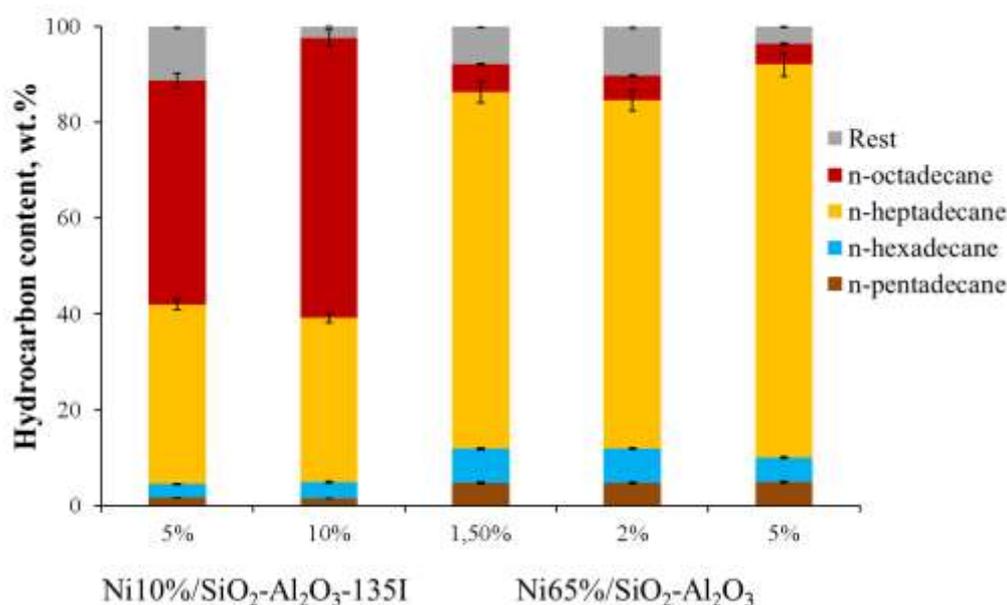

Fig. 2: The effect of catalyst type and amount on dominant hydrocarbon composition. Hydrotreating conditions: operating temperature 340 ºC, initial H$_2$ pressure 100 bar, mixing speed 300 rpm, overall residence time (minimum oxygen removal reaction time from Table 2 + 25 min).

4. Conclusions

Commercial Ni supported catalyst Ni65%/SiO$_2$-Al$_2$O$_3$ has high activity on hydrocarbon production from RO/RFA (weight ratio 1/1) mixture by hydroprocessing. Under studied experimental conditions high yield (76.1%) and ER (90.7%) of marketable hydrocarbon mixture with 96.4% of dominant C$_{15}$-C$_{18}$ content (82 % *n*-heptadecane) was obtained at short overall residence time (~35 min) using 5% of catalyst. Ni10%/SiO$_2$-Al$_2$O$_3$-135I is less active, but opposite to commercial catalyst it produces high *n*-octadecane content (58.4%), which forms in deoxygenation reactions and increases overall yield of hydrocarbons up to 83.2% and ER up to 99.1% using 10% of catalyst amount in ~52 min of hydrotreating process. Studied catalysts have selectivity towards specific hydrocarbons, which is one of the most important feature for consideration of their practical application potential in hydroprocessing of vegetable or animal oil feedstock.

Acknowledgments

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