Experimental Evaluation of Hydrotreated Vegetable Oils as Novel Feedstocks for Steam-Cracking Process

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Abstract: Hydrotreated vegetable oils (HVOs) are currently a popular renewable energy source, frequently blended into a Diesel-fuel. In the paper, HVO potential as feedstock for the steam-cracking process was investigated, since HVOs promise high yields of monomers for producing green polymers and other chemicals. Prepared HVO samples of different oil sources were studied experimentally, using pyrolysis gas chromatography to estimate their product yields in the steam-cracking process and compare them to traditional feedstocks. At 800 °C, HVOs provided significantly elevated ethylene yield, higher yield of propylene and C4 olefins, and lower oil yield than both atmospheric gas oil and hydrocracked vacuum distillate used as reference traditional feedstocks. The HVO preparation process was found to influence the distribution of steam-cracking products more than the vegetable oil used for the HVO preparation. Furthermore, pyrolysis of HVO/traditional feedstock blends was performed at different blending ratios. It provided information about the product yield dependence on blending ratio for future process design considerations. It revealed that some product yields exhibit non-linear dependence on the blending ratio, and therefore, their yields cannot be predicted by the simple principle of additivity.

Keywords: hydrotreated vegetable oil; steam-cracking; olefins production; green chemicals; laboratory pyrolysis

1. Introduction

Biomass is considered a renewable source of energy and automotive fuel. Among all biomass sources, vegetable oils often play a role of a pioneering feedstock because of their similarity to traditional crude-oil-based resources. Specifically, hydrotreated (or hydrogenated) vegetable oils (HVOs), also called "green Diesel", are currently popular for use as components blended into Diesel-fuels [1,2]. Production of HVOs involves catalytic hydro-deoxygenation of triacylglycerols contained in vegetable oils, followed by separation of water and undesired light components [1,3]. Produced HVO then typically represents a mixture of linear-chain alkanes corresponding to fatty acids comprised in form of glycerol esters in the vegetable oil. The resulting mixture has sharp hydrocarbon distribution peaking in C_{17}–C_{18} fractions and contains a small amount of lighter (C_{12}–C_{16}) and heavier hydrocarbons (~C_{20}) formed by side-reactions running during the process [4].

While the exploitation of HVOs as automotive fuels is commonplace nowadays, they should also be considered a potential feedstock for other processes. Since HVOs are formed predominantly by long-chain linear hydrocarbons, they promise high yields of desired products in the steam-cracking process. Steam-cracking of HVOs would be an attractive alternative to their common energetic use. It represents an opportunity to produce green monomers and other green chemicals, specifically petrochemicals, as Kubicka et al. [5] indicated. Besides the hydrotreatment of vegetable oils, significant attention was paid to

hydrotreatment of oil (tar) originated from biomass pyrolysis [6–9]. Derived hydrogenate expresses similar properties as HVOs prepared from primary biomass. Other studies were aimed at catalytic cracking of oils obtained from biomass pyrolysis [10,11]. All mentioned technological pathways lead to the production of fuels, but not chemicals. Methyl-esters of vegetable oils and vegetable oil itself were studied as a potential feedstock for the steam-cracking process [12], but this pathway faces serious technical difficulties given by currently used technology, which cannot handle hydrocarbon feedstock with significant oxygen content due to the formation of carbon oxides during the cracking process. The limitation is given by the arrangement of separation parts of steam-cracking facilities, designed for low content of carbon oxides in the product stream. On the other hand, there is an obvious lack of sources studying the steam-cracking or pyrolysis of HVOs or similar materials mentioned above. There are sparse sources aimed at experimental pyrolysis of pure components, similar to those contained in HVOs. For example, Bartekova and Bajus [13] examined the thermal decomposition of n-hexadecane. However, the conversion was only in the range of 10–50%, which is not comparable to conditions in the process scale. Depeyre et al. [14] investigated n-hexadecane steam-cracking with reaction conditions varying in the wide range. In dependence on conditions, they observed 28.3–100% conversion and ethylene yield up to 48.2 wt.%. Depeyre then extended the study by the modeling of n-hexadecane pyrolysis [15]. Billaud and Freund studied the steam-cracking of a mixture containing C_{12}–C_{20} alkanes, but its composition significantly differs from typical HVO [16]. However, to the best of our knowledge, there is no published study evaluating HVOs as steam-cracking feedstock, nor providing quantitative data needed for consideration before introducing HVOs as feedstock to the industrial scale.

Therefore, the objective of this study is an experimental examination of HVO pyrolysis and a comparison of pyrolysis products' distribution to traditional feedstock for the steam-cracking process. Considering the given nature of HVO (its density and boiling point), atmospheric gas oil (AGO) and hydrocracked vacuum distillate (HCVD) were chosen as traditional feedstocks for the comparison and reference purposes. This comparison should provide a quantitative evaluation of the HVOs as potential steam-cracking feedstock. Our well-established pyrolysis chromatography technique was utilized to achieve these goals. In our previous papers, the technique was established as a laboratory method suitable for studying the effect of feedstock composition on the yield of pyrolysis products, as demonstrated in the example of evaluation of Fischer-Tropsch waxes as a potential feedstock for the steam-cracking process [17]. Furthermore, the effect of light/heavy naphtha blending on its cracking products yield was examined by this technique [18]. It was also applied in a study evaluating the impact of different structural elements on the pyrolysis behavior of individual components [19]. As the technique is markedly sensitive to the feedstock composition, it is an appropriate tool for the intended evaluation. Moreover, a significant correlation was shown between experimental results from the lab-scale pyrolysis and products yields obtained in the process-scale [20].

2. Materials and Methods

2.1. Materials

The samples of HVOs were prepared by the research centre ORLEN UniCRE (Litvínov, Czech Republic) in a pilot scale for HVO testing. Although the current article is focused on the HVOs utilization in the steam-cracking process, not the HVOs' preparation, here we provide a brief description of HVOs' origin, including characterization of vegetable oils, prepared HVOs, and hydrotreatment conditions. However, all the HVO preparation procedures were already published in the previous paper [21]. The feedstocks used for the HVOs' preparation were rapeseed oil (RSO), sunflower oil (SFO), and used cooking oil (UCO). The UCO was supplied by a local waste manager, while SFO and RSO were food quality commercial vegetable oils (provided by ARO). Before the preparation, UCO was filtered using a standard diesel filter to remove solid impurities. Table 1 shows the basic characterization of these materials. The hydrotreating of vegetable oils to produce

HVOs was performed in the same unit used by the authors in previous co-hydroprocessing experiments [21]. The unit is placed in the experimental facility of ORLEN UniCRE a.s., Litvínov-Záluží, Czech Republic. The catalyst bed consisted of commercial hydrotreating sulfide catalysts ($NiMo/Al_2O_3$ and $CoMo/Al_2O_3$). To maintain the catalyst activity constant even during the long-term experiment, it was necessary to add 0.5 wt.% content of dimethyl-disulfide into the raw oils. This served as a continual sulfur source preventing catalyst from deactivation. The sulfur is then in the form of hydrogen sulfide contained in resulting HVOs, which makes the S-content in the HVOs virtually higher than the original content of sulfur in raw oils. Normally, the hydrogen sulfide would be removed from the HVOs after the reactor. Table 2 shows the used operating conditions for the synthesis of HVO with different vegetable oil feedstocks. The HVO obtained at the steady-state was characterized using the same analytical techniques employed for the feedstocks and was stored for its use as a pyrolysis feedstock. The paraffin content in HVO was determined by gas chromatography with a flame ionization detector. Table 3 shows the basic characteristics of the HVOs obtained from the hydrotreating of different vegetable oils.

Table 1. Basic feedstock properties.

Feedstock	UCO	SFO	RSO
Density at [1], kg/m^3	918.3	920.8	920.8
Ref-index [1]	1.4732	1.4750	1.4749
Acid number [2], mg/g	1.13	0.75	0.19
Br-index [2], mg/g	55,384	47,243	42,113
Elemental analysis			
C content, wt.%	76.9	77.6	76.2
H content, wt.%	11.7	11.7	11.7
S content, ppm	4.3	2.1	2.3
N content, ppm	22.3	4.3	2.1
Simdis [3], °C			
10 wt.%	596.20	595.84	596.40
30 wt.%	606.06	605.17	605.90
50 wt.%	609.55	608.83	609.14
70 wt.%	611.83	611.04	611.32
90 wt.%	613.77	612.84	613.08
95 wt.%	616.17	614.76	615.28

[1] Liquid density and refractive index were determined at 20 °C. [2] Acid number and bromine-index were determined in milligrams of reagent (KOH or Br) per gram of sample. [3] Distillation curves obtained by simulated distillation according to standards listed in the text.

Table 2. Description of reaction conditions during HVOs preparation.

Feedstock	T, °C	LHSV, h^{-1}	H_2:Feed, Nm^3/m^3	p, MPa	Catalyst [1]	HVO Sample
Rapeseed oil	340	1	4150	12.5	CoMoS	HRSO1
Rapeseed oil	340	1	4150	12.5	CoMoS	HRSO2
Rapeseed oil	320	2	2400	5.5	NiMoS	HRSO3
Sunflower oil	330	2	2400	5.5	NiMoS	HSFO
Used cooking oil	335	2	2400	5.5	NiMoS	HUCO

[1] Supported by Al_2O_3.

Sample of traditional feedstock, hydrocracked vacuum distillate (HCVD), is a real sample of vacuum residue of hydrocracked vacuum distillate from the crude-oil distillation supplied by Uniperol RPA (Litvínov, Czech Republic). The second traditional feedstock, atmospheric gas oil (AGO), is a real AGO sample from primary crude-oil distillation, which underwent hydrodesulfurization and the following stabilization and was obtained from the same facility. Both samples represent the steam-cracking feedstock in the mentioned facility, where the HCVD is processed on a much larger scale than AGO. The characterization of these samples is provided in Table 3.

Table 3. Basic properties of traditional (HCVD and AGO) and HVOs (hydrotreated rapeseed oil HRSOx, hydrotreated sunflower oil HSFO and hydrotreated used cooking oil HUCO) feedstock for pyrolysis experiments.

Variable	HCVD	AGO	HRSO1	HRSO2	HRSO3	HSFO	HUCO
Density [1], kg/m^3	-	852.6	753.0	752.9	761.3	761.0	762.0
Ref-index [1]	-	1.4759	1.4203	1.4204	1.4264	1.4263	1.4267
Acid number [2]	-	0.04	0.02	0.02	0.02	0.02	0.02
Br-index [2]	-	8534	-	-	4486	4834	3532
Elemental							
C, wt.%	-	86.1	85.0	84.9	84.0	85.0	85.1
H, wt.%	-	13.3	15.0	15.1	15.0	14.6	15.0
S, ppm	-	12000	2.5	2.5	21.8	41.0	26.3
N, ppm	-	232	0.5	0.5	0.5	0.5	0.5
Simdis [3], °C							
10 wt.%	345.1	206.1	295.6	295.8	300.4	300.0	299.7
30 wt.%	390.8	256.8	305.4	306.1	304.6	304.3	304.2
50 wt.%	419.0	289.5	310.2	311.6	310.5	315.1	308.2
70 wt.%	448.8	318.0	320.5	321.4	319.6	319.8	319.3
90 wt.%	494.3	359.7	323.1	324.3	323.4	327.6	324.9
95 wt.%	512.5	378.2	330.3	330.9	352.6	355.5	365.4
Paraffins							
n-C$_{15}$, wt.%	-	-	2.09	2.03	2.56	2.56	3.33
n-C$_{16}$, wt.%	-	-	2.65	2.65	2.39	2.77	3.04
n-C$_{17}$, wt.%	-	-	36.97	36.57	47.53	43.33	47.77
n-C$_{18}$, wt.%	-	-	42.24	42.97	41.75	44.62	41.10

[1] Liquid density and refractive index were determined at 20 °C, [2] Acid number and bromine-index were determined in milligrams of reagent (KOH or Br) per gram of sample. [3] Distillation curves obtained by simulated distillation according to standards listed in the text.

All samples were analyzed using simulated gas chromatography distillation (SIMDIS) following ASTM D2887 for samples with a boiling point up to 520 °C and ASTM D6352, D7169, D1160, and D2892 for samples with a boiling point higher than 520 °C. Density, refractive index, and the acid number of samples were measured according to ASTM D4052, D1218, and D664. Elemental analysis was performed according to ISO 29,541 for the characterization of both vegetable oils and HVOs. The content of sulfur and nitrogen was determined according to ASTM D1552 and D5291.

2.2. Procedures

All samples for pyrolysis experiments were melted and homogenized. The pure feedstock samples were used without any modification, while the blended samples were prepared by differential weighing of components into 10-mL vials with content 10, 20, 40, 60, and 80 wt.% of HVO in HCVD, or 10 wt.% of HVO in AGO. Prepared samples were maintained cold and stored until needed for experimentation. Before the experiment, prepared samples were melted and then maintained liquid at 60 °C in the thermostatic block.

Pyrolysis experiments were performed using the laboratory pyrolysis unit (Shimadzu Pyr-4A), directly connected to two gas chromatographic units (Shimadzu GC-17A) for the separation of products on the system of switched columns and detection on flame ionization detectors. The pyrolysis reactor is a straight quartz plug-flow reactor 18 cm long, 2.9 mm in diameter, filled by SiC, placed in an electrical furnace. A control system limits the peak of the parabolic temperature profile. The apparatus allows quantitative determination of all pyrolysis products C$_1$–C$_6$ individually, the most important products C$_7$–C$_{10}$ and the rest of the reaction mixture forming the oil C$_{11}$+. The method was explained in deep detail and validated on pyrolysis data in our former paper [19]. Furthermore, the reproducibility and accuracy of the experimental technique were determined on an extensive dataset obtained from naphtha pyrolysis experiments [22].

The reactor was operated under 400 kPa and 800 °C with a 65 NmL/min carrier-gas flow (nitrogen). Residence time at the hot zone is 0.35 s under these conditions [18,23]. These conditions were selected as the standard conditions on the apparatus, allowing the comparison of obtained results with an extensive database of already measured data. Samples were fed as a liquid into the reactor in the amount of 0.2 μL by micro-syringe. The injected sample is vaporized and passes through the reactor (plug flow) as an undiluted pulse of the reaction mixture. Pyrolysis products are then carried into the analytical system in the flow of carrier gas (nitrogen), where their separation occurs as well as a final determination on detectors. Our results report the composition of product stream as products mass fractions, which are referred to as process yields (Y). Notably, this definition of yields may differ from the traditional chemical engineering one; it is widely used in papers related to steam-cracking process. Since experiments were repeated (3×), we report ranges of product yields in plots. These ranges shown as error bars represent the minimum-maximum range of the displayed variable obtained from experiments.

3. Results

The summary and discussion of experimental results obtained during the study are divided into two sections. At first, the results of pure feedstocks pyrolysis are presented, and the desired comparison of HVOs to traditional feedstocks is performed. Presented results are discussed in the context of other experimental work with similar feedstock at the end of the first part. In the next part, results obtained in experiments with the blended feedstocks are presented and discussed. Data obtained from pyrolysis experiments as the composition of product stream are shown and discussed as yields of individual products; error bars represent range min-max from repeated experiments.

3.1. Pure Feedstocks Pyrolysis

Here we report the analysis of experimental data to evaluate HVOs as a potential feedstock for the steam-cracking process compared to traditional feedstocks, HCVD, and AGO. The most important products are ethylene and propylene, followed by desired C4 fraction and benzene, in the steam-cracking process. On the contrary, pyrolysis oil is generally not desired product [24]. A simple comparison of the main pyrolysis products yield is provided in Figure 1. The experiments were carried out under constant reaction conditions with all the studied feedstocks. The pyrolysis of HVOs provided a remarkably elevated yield of ethylene (39.9–45.6 wt.%) compared to both traditional feedstocks, HCVD (30.0 wt.%) and AGO (19.8 wt.%), at reaction temperature 800 °C. HVOs also provided a significantly higher yield of propylene (18.7–19.2 wt.%) than HCVD (15.3 wt.%) and AGO (11.3 wt.%), and a higher yield of C4 fraction (15.2–18.2 wt.%) than ones obtained of HCVD and AGO (14.9 wt.% and 8.3 wt.%). Moreover, the pyrolysis oil yield was significantly lower in all cases of HVOs (1.5–3.6 wt.%) compared to both HCVD and AGO (9.7 and 28.1 wt.%). On the other hand, the yield of benzene obtained from HVOs (1.3–3.4 wt.%) is lower than that of HCVD (3.9 wt.%) and approximately comparable to AGO (2.7 wt.%). Besides the decreased yield of benzene, all trends mentioned above are beneficial.

The differences in the HVOs' composition (see Table 3) are not large enough to expect any significant difference in their pyrolysis behavior, but the yields are surprisingly different. As evident from Figure 1, HRSO1 provided higher yields of ethylene and C4 fraction and a lower yield of benzene than all remaining HVO samples. Both HRSO1 and HRSO2 samples were obtained from rapeseed oil during the same long-term experiment of HVO preparation and under the same conditions. The HRSO2 sample was collected after the preparation process safely achieved steady-state, but the sample HRSO1 was collected much later. This fact is the only known difference between these two samples. We assume that catalyst deactivation influenced the preparation process and consequently caused these two samples to differ in composition. Despite no significant difference analytically determined in these two samples' composition, they still can differ in the part of mass "invisible" for the performed analytical techniques, namely, non-linear alkanes.

The relatively many differences between studied samples also document the merit of the pyrolysis chromatography technique utilization to characterize the samples, as this technique can reveal the differences that would be normally difficult to detect by standard analytical techniques. The next interesting fact is that the HUCO sample provided the lowest yield of ethylene of all HVOs samples and a lower yield of C4 fraction compared to HRSO1 and HRSO2. All remaining differences between HVOs can be considered not significant. We believe the explanation above is valid also for those two samples.
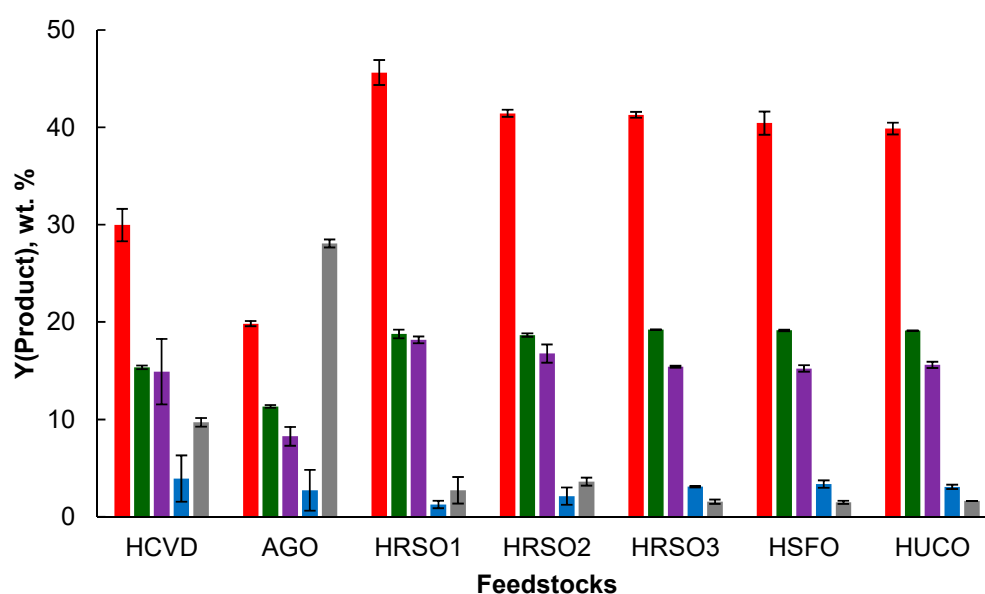

Figure 1. Yields of main pyrolysis products: ■ ethylene,■ propylene, ■ C4 fraction, ■ benzene and ■ oil obtained from pure feedstock pyrolysis under constant reaction conditions (400 kPa, 800 °C, 65 NmL/min).

The pyrolysis behavior of HVOs has not been studied prior to our study. Therefore, we decided to extend our study of its behavior by analyzing yields sensitivity to reaction temperature. Here we demonstrate the temperature dependency of pyrolysis products' yield on the example of HRSO1. The behavior of remaining HVOs in dependence on reaction temperature was similar. In Figure 2, the yield of the selected products of HRSO1 obtained under various reaction temperature is shown, while all other variables remain constant. As it is clearly visible, the yield of light products increases with increasing temperature, and this increase is approximately convex in the case of ethylene. In contrast, the increase of methane, propylene, and butadiene is concave at higher temperatures. Therefore, we can estimate that these products approached maximum. It testifies that the reaction temperature is approximately optimal, and with more increased temperature (or residence time), HVO would become "overcracked".

Based on data obtained during the products' chromatographic analysis and the recorded chromatograms, we confirm that peaks belonging to main components of HVOs (n-paraffins) were visible on the FID detecting oil fraction when the sample underwent low-temperature experiments (725–700 °C). Therefore, non-converted HVOs are just included in the oil fraction of products. But at 800 °C, these peaks disappeared in the mixture of pyrolysis oil, which indicates that the conversion of HVO is approaching total conversion at 800 °C.

As stated in the introductory section, we did not find any source focused on the experimental investigation of HVO pyrolysis. However, Depeyre et al. [14] investigated the pyrolysis of n-hexadecane, which is structurally similar to C_{17}–C_{18} paraffins contained in HVOs. When Depeyre approached the total conversion of n-hexadecane (95–100%) at temperatures 750–800 °C, ethylene yield varied in the range 41.3–47.6 wt.% depending on dilution of feedstock by steam, and therefore with varying residence time (0.6–1.0 s).

This ethylene yield approximately fits our data. In the middle of this conditions subrange, under total conversion, Depeyre observed yields ~43 wt.% of ethylene, ~12 wt.% of propylene, ~2.5 wt.% of benzene, and ~6 wt.% of C4 fraction that approximately agree with our results. This provides partial validation of our data, even though they were obtained by experimentation with only similar feedstock, on significantly different equipment, but under comparable feedstock conversion and with similar ethylene yield. Another support can be taken from Billaud and Freund [16]. They cracked a C_{12}–C_{20} alkanes mixture, at which C_{14}–C_{17} formed 89%, and they obtained 42.4 wt.% of ethylene, 18.4 wt.% of propylene, 16.8 wt.% of C4 faction, 1.8 wt.% of benzene, and ~1 wt.% of oil at 780 °C.
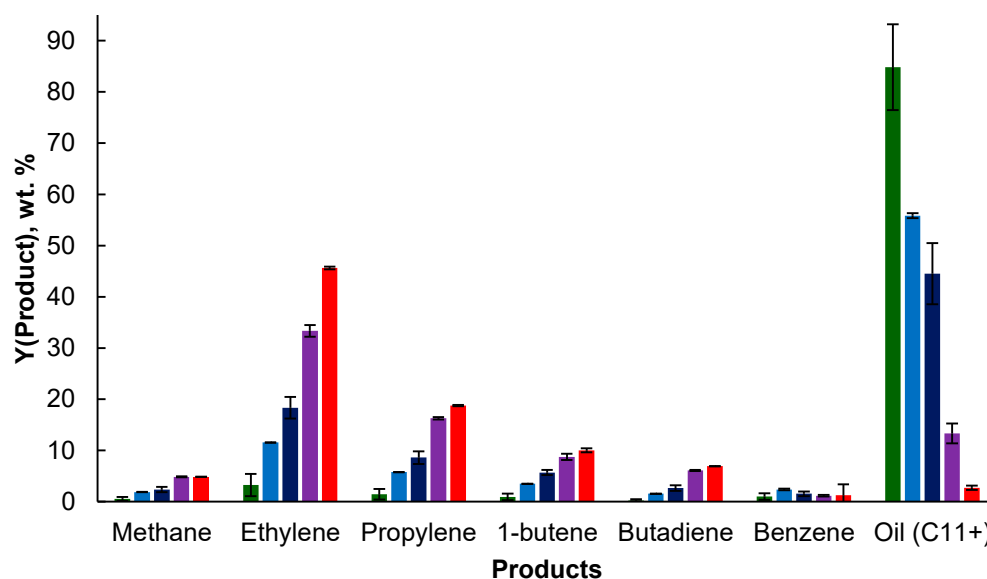

Figure 2. Selected products yield of HRSO1 pure feedstock pyrolyzed under 400 kPa, 65 NmL/min and various temperature: ■ 700 °C, ■ 725 °C, ■ 750 °C, ■ 775 °C, and ■ 800 °C.

3.2. Blended Feedstocks Pyrolysis

It is expected that for pilot testing or process-scale experiments, an industrial producer cannot allocate the full capacity of the steam-cracker (typically 20–30 t/h), or such a large source of HVO may not be available. Therefore, we decided to investigate the pyrolysis of blends containing HVO blended into HCVD or AGO on selected examples. It will provide a quantitative evaluation of blends as the input material for the steam-cracking process.

With respect to previously presented results, HRSO1 and HRSO2 were selected as example feedstocks due to their high yield of light products and the availability of rapeseed oil. HCVD was selected as a traditional feedstock due to its common use by our industrial partner. In Figure 2, there are yields of main products shown in dependence on the content of HVO (HRSO1 or HRSO2) in the blend with HCVD. The results were obtained under the constant reaction conditions. The dependence over the whole blending ratio clearly shows general trends: yield of light olefins (ethylene, propylene and C4 fraction) increases with the increasing content of HVO in the feedstock, and the yield of oil significantly decreased over the blending ratio.

While previously commented trends seem to be approximately linear, benzene yield expressed an interesting trend: starting from the 3.9 wt.% (for pure HCVD), a maximum >5 wt.% of benzene was achieved around content ~20 wt.% of HVO in the blend, and then decreased again with higher content of HVO in the feedstock to final benzene yield for pure HRSO1 or HRSO2 (2.1 or 3.1 wt.%, resp.). This could be caused by the fact that both feedstock components produce benzene, but through different mechanisms, and therefore in different quantities. HCVD contains substituted saturated cyclic and polycyclic hydrocarbons, and these provide benzene by dealkylation. At the same time HVO can form the benzene as a secondary product from ethylene and butadiene, which are both formed with high yields

from HVO. It can be hypothesized that around 20 wt.% of HVOs, the feedstock composition is suitable for benzene formation with maximal yield from both components present in the feedstock under these conditions.

Even the 10 wt.% content of both HVOs in the feedstock slightly improved the yield of the main products, as visible in Figure 3. In Table 4, there are listed yields of products from experiments done under constant conditions for both pure traditional feedstocks, all pure HVOs followed by mixtures containing 10 wt.% of HRSO1 or HRSO2 blended in HCVD or AGO. In contrast to the already presented results, Table 4 provides products distribution in full detail. For example, it was already discussed that HVOs generally provided a high yield of C4 fraction, which is one of the desired side-products of the steam-cracking process. The most desired components of C4 fractions are butadiene and 1-butene. According to the data in Table 4, summed content of 1-butene and butadiene is 14.3–17.0 wt.% for HVOs, while only 12.6 wt.% and 6.6 wt.% for HCVD and AGO. Therefore, the C4 fraction obtained of HVOs in more significant amounts is more valuable than that of HCVD and AGO. It is also visible that the benzene yield obtained from 10% blends (4.1–4.7 wt.%) is higher than benzene yield obtained from pure HVOs (1.3–3.4 wt.%) as well as both traditional feedstock HCVD and AGO (3.9 and 2.7 wt.%). Detailed composition table also provides yields of toluene, xylenes, styrene, and naphthalene. Toluene, xylenes, and styrene are usually not isolated as steam-cracking products, but rather they are reprocessed by hydrodealkylation to benzene (or by a similar process), which finally leads to their beneficial use. From this perspective, it would also be beneficial to process HCVD or AGO feedstock with only 10 wt.% content of HVO, since these mixtures provided a higher yield of ethylene, propylene, and C4 fraction than HCVD or AGO, but also elevated yield of benzene, and elevated or equal summary yield of toluene, xylenes, and styrene.
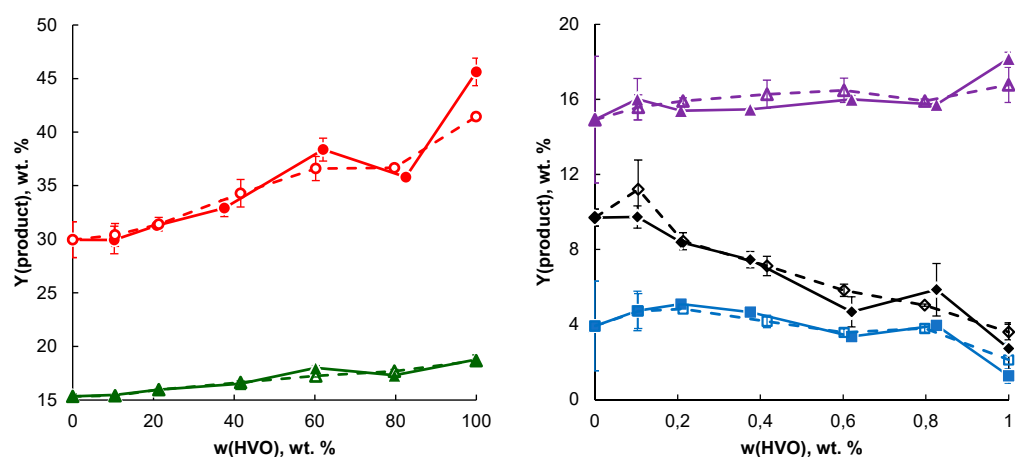

Figure 3. Pyrolysis products yield obtained under constant reaction conditions (400 kPa, 800 °C, 65 NmL/min) in dependence on the HRSO1 (solid, filled) or HRSO2 (dashed, empty) content in feedstock blended in HCVD. **Left**: ○● ethylene, ▲△ propylene, **Right**: ▲△ C4 fraction,■□ C4 Benzene, ♦◇ Oil.

A precise economic analysis should be performed to evaluate the most profitable scenario for the current situation in the merchant products market. There are already established methods available [25] for this kind of evaluation, demonstrated in the example of light/heavy naphtha cracking [18]. It uses total economic value of products produced per one ton of investigated feedstock in relation to the products value obtained from a ton of referential (well known) feedstock, which forms referential economic value. However, such an analysis must consider current or predicted prices of products. We used the same method for the evaluation as in the previous paper [25], and products prices valid for 06/2017 in the central Europe to demonstrate the impact of HVOs to the process economy. Based on experimental results from lab-pyrolysis in the Table 4, and considering the HCVD

as referential feedstock, pure HRSO1 provided strongly positive value 98 EUR/t. It means that HRSO1 pure would provide products with total sale price by 98 EUR/t higher than HCVD. The remaining pure HVOs provided values in range 70–80 EUR/t. The examined content 10 wt.% of HVOs in HCVD, affected the resulting value only slightly, in interval −0.8–1.3 EUR/t. But the same addition of 10 wt.% of HVOs into the AGO caused significant change of products value, by +27 and +25 EUR/t, compared to pure AGO.

Table 4. Products distribution (in wt.%) obtained at 800 °C, under 400 kPa and 65 NmL/min for pure traditional feedstocks (HCVD and AGO), pure HVOs (HRSO1, HRSO2, HRSO3, HSFO and HUCO) and blends containing 10 wt.% of HRSO1 or HRSO2 in HCVD or AGO.

Feedstock	HCVD	AGO	HRSO1	HRSO2	HRSO3	HSFO	HUCO	HRSO1 +HCVD	HRSO2 +HCVD	HRSO1 +AGO	HRSO2 +AGO
Methane	5.2	6.3	4.9	6.1	7.1	7.2	7.0	5.5	5.4	6.1	5.9
Ethane	1.5	1.8	1.5	1.9	2.7	2.9	2.9	1.6	1.7	1.6	1.5
Ethylene	30.0	19.8	45.6	41.4	41.3	40.4	39.9	29.9	30.4	22.2	22.2
Acetylene	0.6	0.2	0.4	0.3	0.2	0.2	0.2	0.4	0.4	0.2	0.2
Propane	0.6	0.3	0.4	0.5	0.5	0.5	0.5	0.4	0.5	0.3	0.3
Propylene	15.3	11.3	18.8	18.7	19.2	19.1	19.1	15.5	15.4	12.1	12.1
Propa-1,3-diene	0.2	0.0	0.1	0.2	0.2	0.2	0.2	0.0	0.0	0.0	0.0
Propyne	0.5	0.2	0.2	0.2	0.2	0.2	0.1	0.4	0.4	0.3	0.3
i-butane	0.2	0.0	0.4	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-butane	0.3	0.2	0.0	0.1	0.1	0.1	0.1	0.4	0.5	0.2	0.2
trans-but-2-ene	0.0	0.3	0.2	0.0	0.3	0.3	0.3	0.0	0.0	0.3	0.1
But-1-ene	4.8	1.9	10.0	8.2	6.6	6.4	6.8	5.9	5.7	3.0	3.4
i-butene	1.3	0.9	0.3	0.3	0.2	0.2	0.2	1.6	1.6	1.4	1.4
cis-but-2-ene	0.4	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.3
Buta-1,3-diene	7.9	4.7	6.9	7.7	7.9	7.9	7.8	7.6	7.5	5.1	5.1
CPD	2.4	1.3	0.7	1.5	1.5	1.6	1.5	3.0	2.7	2.2	2.2
C$_5$–C$_7$ non-id.	7.3	7.2	3.4	4.9	4.5	4.8	5.4	4.6	4.0	3.2	3.4
Benzene	3.9	2.7	1.3	2.1	3.1	3.4	3.1	4.7	4.7	4.4	4.1
Toluene	2.7	3.3	0.3	0.0	0.9	1.0	1.0	2.7	1.6	2.9	2.7
EB	0.2	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0
m+*p*-xylenes	0.7	1.3	0.0	0.0	0.1	0.1	0.1	0.9	0.9	1.2	1.2
Styrene	1.0	1.5	0.3	0.0	0.5	0.5	0.5	1.0	1.0	1.3	1.3
Naphthalene	0.4	1.0	0.0	0.0	0.0	0.0	0.0	0.5	0.3	1.0	0.9
C$_7$–C$_{12}$ non-id.	2.8	5.3	1.2	1.8	1.0	1.0	1.2	3.2	3.6	4.9	5.1
Oil (C$_{11}$+)	9.7	28.1	2.7	3.6	1.6	1.5	1.7	9.7	11.2	25.6	26.0

4. Conclusions

Hydrotreated vegetable oil (HVO) is currently widely applied as a renewable energy source, mainly as a component of Diesel-fuel. However, it is also a very promising feedstock for the steam-cracking process. Our experimental results indicate that HVOs provide much higher yields of desired steam-cracking products, namely ethylene, propylene, and C4 olefins, than comparable traditional feedstocks (HCVD and AGO). Moreover, HVOs provide a significantly lower yield of undesired pyrolysis oil. Based on our comparison of five different HVOs, we estimate that the HVOs' preparation process may influence the HVOs properties and consequently the distribution of steam-cracking products more than the vegetable oil used for the preparation. Markedly, even the HVO prepared from used cooking oil represents interesting candidate feedstock for steam-cracking process. Experimental investigation of blended samples over the whole blending ratio with HCVD revealed that several products exhibit non-linear dependence on the blending ratio, and therefore, their yields cannot be predicted by the simple principle of additivity. Blends containing 10 wt.% of HVO in traditional feedstock showed slightly enhanced product yields, but the difference is more significant when HVO is blended into the AGO than HCVD. The blended samples investigation provided information about the product yield dependence on blending ratio for future process design considerations.

Abbreviations and Symbols

LHSV	h^{-1}	Liquid hourly space velocity
p	kPa, MPa	absolute pressure
T	°C	temperature
w(i)	wt.%	mass content of component *i*
Y(i)	wt.%	yield (in the sense process yield of product *i*)
AGO		atmospheric gas oil
HCVD		hydrocracked vacuum distillate
HVO		hydrotreated vegetable oil
RSO		rapeseed oil
SFO		sunflower oil
SIMDIS		simulated gas chromatography distillation
UCO		used cooking oil

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