Petroleum and Coal

HYDROGENATION OF LIQUID HYDROCARBON FRACTIONS FOR PRODUCTION OF NON-CONVENTIONAL DIESEL FUEL

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Abstract

Study of kinetics during hydrogenation of hydrocarbon fractions prepared by pyrolysis of waste plastic is presented. Fractions were separated by distillation from oily/wax depolymerizates obtained during pyrolysis of polyethylene and polypropylene from end-of-life vehicles at 450°C in the batch reactor. The hydrogenation of liquid fractions in the boiling range of diesel was studied as a way of upgrading before their addition into fossil diesel fuels. Optimized experimental conditions of hydrogenation and optimized conditions for chromatographic separation are reported. The success rate of hydrogenation based on the alkane/alkene ratio in the samples after hydrogenation was evaluated by chromatography and by IR spectroscopy. Finally, the selected properties prescribed in fuel standards before and after hydrogenation are compared.

Keywords: *polyalkene recycling; hydrogenation; diesel fuel; kinetic study; used cars.*

1. Introduction

The global energy sector, as well as the economy, is still largely based on non-renewable fossil fuels (oil, natural gas, coal). Growth in oil prices creates favourable conditions for renewable energy and recycling technologies. An increasingly important area of recycling technology is becoming waste plastics processing technology, which reflects the fact that the amount of waste plastics produced (50% of annual plastic production: 150 million tonnes [1]) has only a smaller value than the annual production of medium-range petroleum distillates (world-wide daily production [2]).

Interesting is the situation in the automotive industry. In the EU countries, approximately 6 million cars per year become a feedstock for recycling due to the end of their live [3]. The weight of plastic in one car in 2010 amounted to 130 kg, and this number is steadily growing. EU legislation, which came into force on 1 January 2015, aims to increase the recyclability of car parts after the end of life up to 95% of the weight of the vehicle. Polypropylene (17%) and polyethylene (4%) make up the second largest proportion of different types of plastics used in the automotive industry [4]. It is generally known that polyalkenes are the most suitable raw materials for chemical conversion to automotive fuels or chemical feedstock [5].

Pyrolysis, thermal decomposition in the absence of oxygen and the absence of catalysts is a known and technologically controlled process of chemical conversion of polyalkenes to motor fuels [6]. The disadvantage of pyrolysis is the dependence of the quality and amount of individual pyrolysis fractions on the properties of polyalkenes, the type and amount of auxiliary compounds present (e.g., fillers, stabilizers), pyrolysis reactor parameters and pyrolysis conditions [7]. The products of cracking of waste polyalkenes have an unsaturated character and, depending on the additives used in the manufacture of plastics, may also contain sulphur or nitrogen compounds [5, 8].

Hydro-refining belongs to the chemical refining processes which remove unwanted substances from the hydrocarbon fractions. The bonds contained in the unsaturated hydrocarbons are saturated during hydrogenation using suitable catalysts in a hydrogen atmosphere. The unsaturated hydrocarbons are changed to saturated, cyclopentanes are converted to isoalkanes, and the aromatics are hydrogenated to cyclohexanes. The rings are gradually saturated and opened in polycondensed aromatics. Oxygenates, sulphates and nitrogenous substances change gradually through hydrogenation to hydrocarbons, water, sulphate, and ammonia. It is easier to decompose the oxygen and the worst the nitrogen contained substances. The course of the reactions strongly depends on the hydrogenation reaction conditions and the type of used catalyst. The hydrogenation components of the catalysts are metals (Pt, Pd, Ni, Co), their oxides and sulphides. Hydrogenation refinements of the light products are carried out in the vapour phase, liquid or mixed phase. Working conditions may vary depending on the raw material, catalyst, and quality requirements.

Diesel fuels are produced from crude oil fractions, which do not contain unsaturated hydrocarbons. In the case of addition of liquids prepared by pyrolysis of plastics to the diesel fraction, unsaturated hydrocarbons formed during thermal decomposition will decrease the cetane number and worsen colour and oxidation stability of the fuel mixture. For this reason, we have studied the kinetics of hydrogenation of unsaturated hydrocarbons present in products after pyrolysis of waste polyalkenes. The results of hydrogenation should be the better colour stability of liquid motor fuel, smell, and better combustion properties.

2. Experimental

2.1. Feedstock

Waste polyethylene (PE) and polypropylene (PP) derived from used cars were used for feedstock recycling by pyrolysis in a batch reactor at 450°C. Obtained oil/wax liquid products were separated into fractions by laboratory distillation apparatus. The liquid depolymerizates were first fractionated under atmospheric pressure up to 180°C. Distillation of the residue continued under reduced pressure (1.9 kPa) up to the distillation temperature of 190°C, what corresponds to the temperature of 330°C after calculation to the atmospheric pressure. Prepared distillation fractions with the boiling range of 180 to 330°C correspond to the diesel fuel range, and they were used for subsequent hydrogenation reactions. The detailed description of the laboratory reactor is given in study [5].

2.2. Hydrogenation

The hydrogenation was carried out in a batch, mechanically stirred (magnetic transfer, stirrer) pressure reactor. Reactor with volume approx. 100 mL was electrically heated in the shell, and they had a bottom outlet valve with a built-in sampling filter. A powdered hydrogenation catalyst of 3.5% palladium on charcoal was used, which was activated at 300°C for 3 hours before the reaction. Optimized conditions of hydrogenation for individual samples are shown in Tab. 1.

Table 1. Optimized hydrogenation conditions

Parameter / sample	PE	PP
Sample weight, g	55 and 34	50 and 39
Catalyst weight, g	3 and 2	6, 6.6 and 5
Reaction temperature, °C	110 – 120	
Reactor pressure, MPa	1.77 – 2.16	
Reaction time, h	5 and 6	13 and 14.5
Stirrer speed, rpm	600 – 1100	

2.3. Gas chromatography

For the analysis of the liquid samples, the Agilent Technologies 7890A GC gas chromatograph with FID detector and HP-5 capillary column (30 m x 0.32 mm, 0.25 µm) was used. A

linear temperature program from 30°C with a ramp of 5°C/min to 200°C and a ramp of 8°C/min to 330°C was applied. Amount of sample represented 0.2 µL, and it was injected into the split/splitless inlet heated to 350°C. For selected samples, components were identified by mass spectrometry (MS, Agilent Technologies, MS 5975C).

2.4. FTIR spectroscopy

Infrared spectra were obtained using a Genesis FTIR spectrometer (Mattson-Unicam) in the 400-4000 cm^{-1} wavelength range (64 scans, 4 cm^{-1}). Liquid samples were measured in a KBr cell of 0.1 mm thickness and thoroughly washed with anhydrous solvents before measurements.

3. Results and discussion

3.1. Kinetics of hydrogenation

The change in composition and the decrease in the double bond content of the PE and PP samples during hydrogenation was monitored by gas chromatography (GC) using optimized conditions for a good separation of components in liquids. During the hydrogenation, small amounts of sample were taken at regular intervals for GC analysis. For PE liquids, samples were analysed at 1, 2, 3, 4 and 5 hours after the start of the reaction, and the resulting product after approx. 5.33 hours of hydrogenation (PEH). It was more difficult to hydrogenate the liquid from PP pyrolysis under the given conditions. For the analysis of the decrease of the double bonds, sampling was used for longer periods of time: after 2, 4, 6, 8 and 9.25 hours from the start of the hydrogenation and the resulting hydrogenate after 14 hours of reaction (PPH).

The peaks of the unsaturated compounds and their saturated counterparts were selected from the first part (so-called light hydrocarbons) and from the last part (so-called heavier portions) of the chromatogram which have the same number of carbon atoms. These compounds were identified with great certainty based on MS spectrometry and based on available chromatographic data for a similar mixture of compounds from pyrolysis [9]. The peaks of the compounds with the highest weight, meeting the above conditions were also observed and identified. The identified compounds and their retention times are listed in the Tab. 2 and Tab. 3.

Table 2. Identified compounds for monitoring kinetics of PE products hydrogenation

	Label	Retention time /min	Compound	Molecular formula	Mole weight / g mol^{-1}
Light fraction	PE1	7.30 – 7.32	*1-decene*	C10H20	140.27
	PE2	7.53 – 7.55	*decane*	C10H22	142.28
	PE3	7.69 – 7.72	*2-decene*	C10H20	140.27
	PE4	7.93 – 7.95			
Main fraction	PE5	21.18 – 21.19	*1-pentadecene*	C15H30	210.24
	PE6	21.39 – 21.42	*pentadecane*	C15H32	212.25
	PE7	21.49 – 21.52	*2-pentadecene*	C15H30	210.24
	PE8	21.73 – 21.76			
Heavy fraction	PE9	35.75 – 35.77	*1- docosene*	C22H44	308.34
	PE10	35.85 – 35.86	*docosan*	C22H46	310.36
	PE11	35.91 – 35.94	*2- docosene*	C22H44	308.34
	PE12	36.13 – 36.15			

The variations in the peak area of the test compounds during hydrogenation are shown in Fig. 1. Alkene peak areas are clearly declining with the time of hydrogenation, on the contrary, the areas of the peaks of the counterpart alkanes in the case of PE are growing. From the signal intensities for the different chromatogram areas, it can be seen that the peak of the compounds at the beginning and at the end of the chromatogram are significantly smaller than the peak intensities of the compounds with the largest proportion. Also, from the similarity of peaks at the beginning and end of the chromatogram, a certain symmetry of the distribution and the peak heights of the compounds results. This is obvious in the case of a PE

sample where the intensity of the main alkanes/alkene peak drops predictably with a decreasing number of carbons from the most intense alkane (C15) and the increasing number of carbon from the most intense alkane (C15). The more complex is the chromatogram for the PP sample, which can also be seen in Fig. 1 for the heavy fraction of PP. This is caused by a larger number of formed mainly branched alkanes and alkenes.

Table 3. Identified compounds for monitoring kinetics of PP products hydrogenation

|	Label	Retention time /min	Compound	Molecular formula	Mole weight/g mol^{-1}
Light fraction	PP1	12.70 – 12.72	*2,4,6-trimethyl-1- nonene*	C12H24	168.32
	PP2	12.81 – 12.83	*2,4,6-trimethyl-1- nonene*		
Main fraction	PP3	18.99 – 19.03	*2,4,6,8-tetramethyl-1- un-decene*	C15H30	210.40
	PP4	19.20 – 19.23	*2,4,6,8-tetramethyl-1- un-decene*		
	PP5	19.44 – 19.46	*2,4,6,8-tetramethyl-1- un-decene*		
Heavy fraction	PP6	29.08 – 29.11	*2,4,6,8,10,12-hexamethyl-1- pentadecene*	C21H42	294.56
	PP7	29.67 – 29.71	*C21- olefine*		
	PP8	30.33 – 30.38	*C21- olefine*		
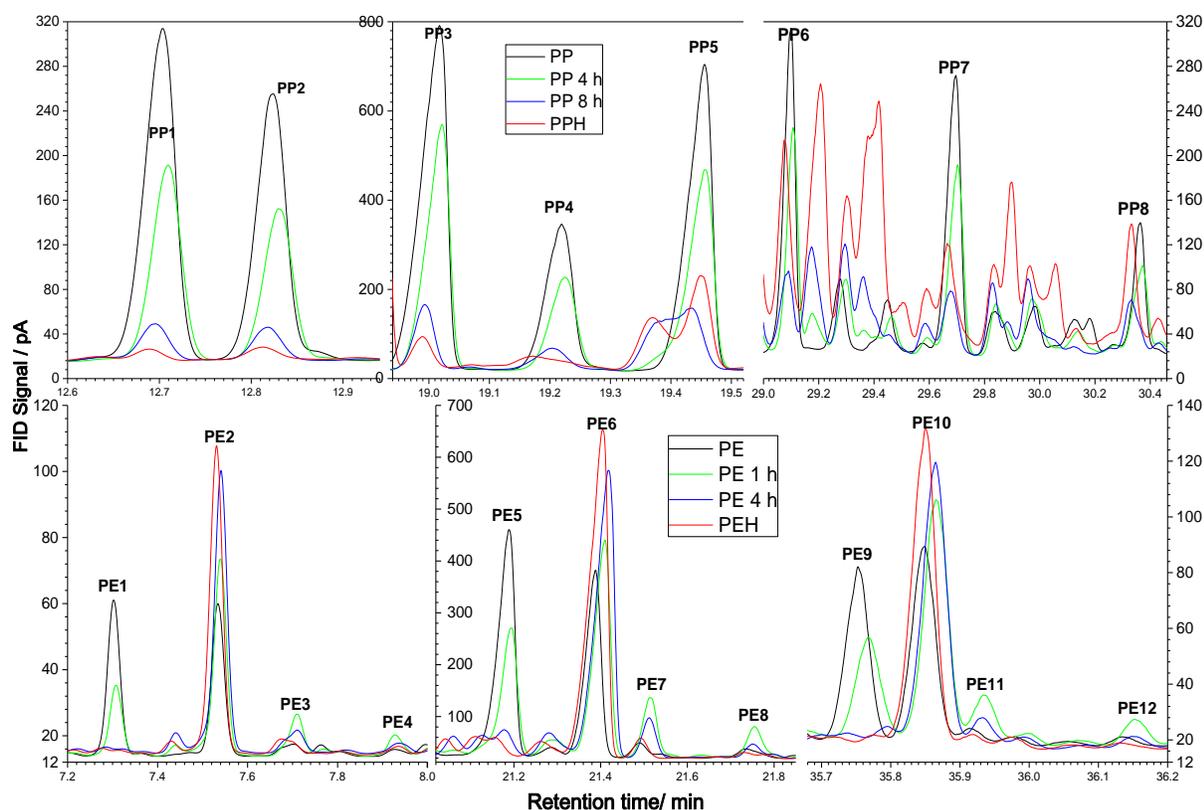
Figure 1. Intensities of selected peaks with increasing hydrogenation time for PE liquid hydrogenation (below) and PP samples (top)

The kinetics of hydrogenation of the PE sample was processed using the time-dependent conversion of a number of alkenes with a given number of carbon to the corresponding alkane (X_{alkene}). We calculated the X_{alkene} values based on the sum of the peak areas of the selected

alkenes with the same number of carbons (in particular for C10, C15, C22) to the peak area of the corresponding alkane. In the case of PE, they are all linear hydrocarbons. Another characteristic for hydrogenation kinetics, even in the case of a PP sample, was the time dependence of alkenes with a given number of carbons expressed as a percentage by weight (w). We obtained w values by the sum of the area of the selected alkenes with the same number of carbon atoms (C10, C15, C22 for PE and C12, C15, C21 for PP) to the total area of all peaks of the sample.

The rapid drop in double bonds during PE hydrogenation correlates with a decrease in the ratio of alkenes to alkane X_{alkene}. Alkene predominates before hydrogenation; for C15, about 56 % is alkene; for C10 the ratio is equal. At the end of the hydrogenation, the alkene content of the C10, C15 and C22 carbons is less than 10 %. A similarly strong decrease is also observed with the percentage of alkenes (w) C10, C12, and C22. These experimental dependencies except w (C22) can be reliably described by exponential trends with a correlation coefficient greater than 0.96. This indicates the overall behaviour of the kinetics of C10 and C12 alkenes hydrogenation occurs according to the first order. Hydrogenation of longer C22 chains shows different kinetics, a slight increase in hydrogenation rate can be seen on the w (C22) curve, after 6 hours there is a break and a more severe decrease in the double bond content.
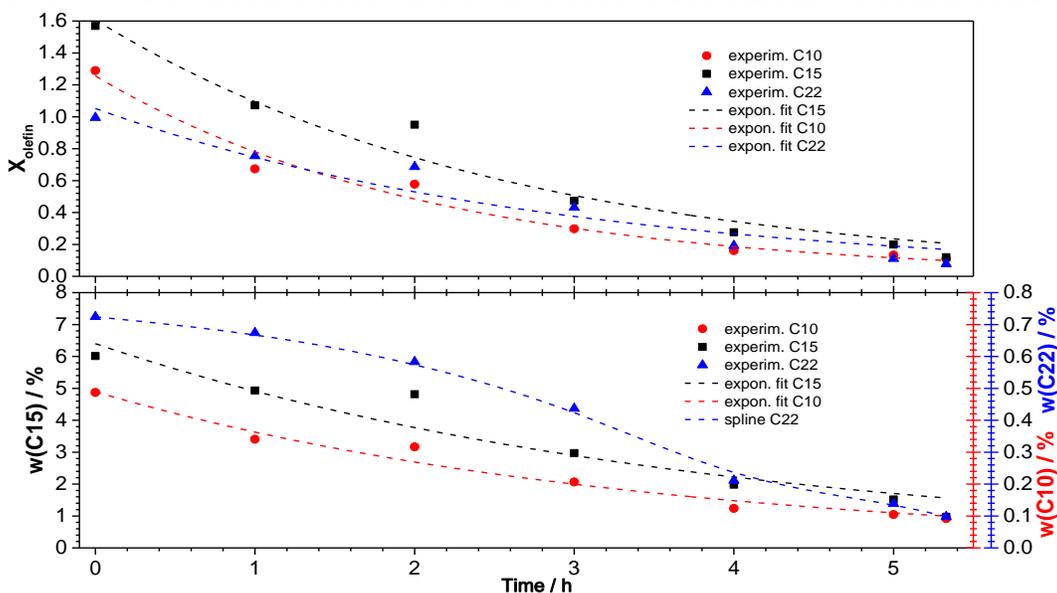

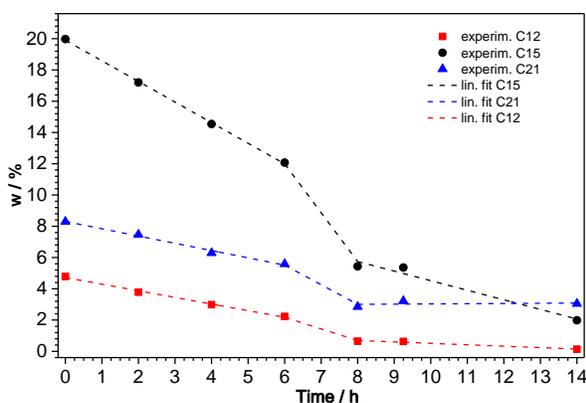Figure 2. Kinetics of hydrogenation of the PE sample based on X_{alkene} and w

Figure 3. Kinetics of PP hydrogenation based on w values

Unlike the PE sample, kinetics of hydrogenation of the PP sample were studied only based on *w* values. The mass fraction of each selected alkenes is much larger than for a similar number of carbon in the case of PE. From the point of view of the trend of the double bond kinetics, the PP sample manifests itself as according to the kinetics of the zero order. It shows the linear character of the decrease of the double bonds with the time of hydrogenation (correlation coefficient greater than 0.92). At 6 hours there is a break and then continues again with a linear decrease in character. Evidently, it results from the w values that the hydrogenation of the PP sample compared to the hydro-

genation of the PE sample is significantly slower. While the average number of selected double bonds of PP samples drops after 6 hours of hydrogenation by 42 %, in the case of PE samples, this drop by 49 % in only 3 hours of hydrogenation.

3.2. Overall assessment of hydrogenation

The success of hydrogenation can be evaluated based on a change in the total alkene/alkane ratio for selected PE compounds and by the decrease in weight fraction of selected alkenes before and after hydrogenation (both samples PE and PP). If we calculate the X_{alkene} value (Figure 2, above) for all selected compounds of the PE sample, we arrive at the total ratio of the selected alkene / selected alkanes. This ratio represents 1.46 for the original, non-hydrogenated sample PE, i.e., about 50 % more is alkenes per the corresponding alkane. At the end of the hydrogenation, this ratio drops to 0.11, meaning that the alkanes already prevailed. A similar decrease is observed in the total weight ratio of double bonds (w, analogously to Fig. 2), where before hydrogenation it is 7.2 % and after completion of hydrogenation 1.2 %. Thus, a 90% reduction in the weight fraction of the selected alkenes at the end of the hydrogenation is observed. A similar trend is shown by hydrogenation of the PP sample, where the weight fraction of the selected alkenes before hydrogenation is 33.1 % and at the end of the hydrogenation is 5.2 %, representing an 84 % decrease in selected double bonds.

The degree of hydrogenation of both PE and PP samples was also controlled by IR spectra. As a standard to verify the effect of the presence of double bond on the FTIR spectra, 1-tridecene was used, the spectra of which were compared to the alkane n-tridecane. Fig. 4 clearly shows the bands that occur in the FTIR spectra when one double bond is introduced at the 1-position into the n-alkane. For both the alkane and the alkene spectra, common intensive bands at 2800-3000 cm^{-1} and 1450 cm^{-1}, which correspond to common vibrations in the saturated hydrocarbon moieties, and the absorbance at 720 cm^{-1} corresponds to an n-alkane chain having a carbon number of 5 or more. Relatively intense absorbance at 3077 cm^{-1}, 1640 cm^{-1}, 991 cm^{-1} and 909 cm^{-1} in the 1-tridecene spectrum correspond to vibrations associated with R-CH = CH_2 groups. Also, in the 1-tridecene spectrum, the lower absorbance at 1820, 634 and 552 cm^{-1} are also present.

In the PE sample, in particular, 1-alkenes in a ratio of about 1:1 with linear alkanes, the FTIR spectra should be close to the 1-tridecene spectrum. In Fig. 4 for the PE sample the intensive absorbance at 3077 cm^{-1}, 1641 cm^{-1}, 991 $cm^{-1,}$ and 909 cm^{-1} are found to correspond to the double bond in the 1-tridecene. Also less intensive bands at 1821 cm^{-1}, 634 cm^{-1} and 552 cm^{-1} copy the 1-tridecene spectrum. In the FTIR spectra of the hydrogenated PEH sample (Fig. 4), the majority of the strips, corresponding to the presence of the double bond, are reduced to complete extinction. The ratio of integral areas of PEH sample to PE samples for the double bond bands results in 85% conversion of the double bonds. This result is in good agreement with the 90 % conversion of alkenes to alkanes obtained by gas chromatography.

The FTIR spectrum of the PP sample is something more complex than in the previous case, because branched hydrocarbon chains result in more complex spectra, especially in the 700-1,500 cm^{-1} range. Since we did not have a standard for branched alkenes, we compared the spectra with baseline absorbance at 3077 cm^{-1} and 1649 cm^{-1}. Other absorbance corresponding to double bonds are significantly covered by the absorbance of branched hydrocarbon structures, especially in the range of 700-1200 cm^{-1}, and are also slightly shifted. Absorbance at 3077 cm^{-1} decreased significantly, but a slight indication of its presence is still visible on the 2800-3000 cm^{-1} strong shoulder. Absorbance at 1649 cm^{-1} also dropped significantly after hydrogenation.

Similarly, the absorbance at 1821 cm^{-1} and 560 cm^{-1} decreased. By comparing the integral areas for the double bond strips, we proceed to 75 % conversion of the double bonds of the PP sample at the end of the hydrogenation. This result also correlates with the result of chromatographic conversion (84 %), but for the above-mentioned reasons of branched hydrocarbon formation, these results are expected to have greater differences.
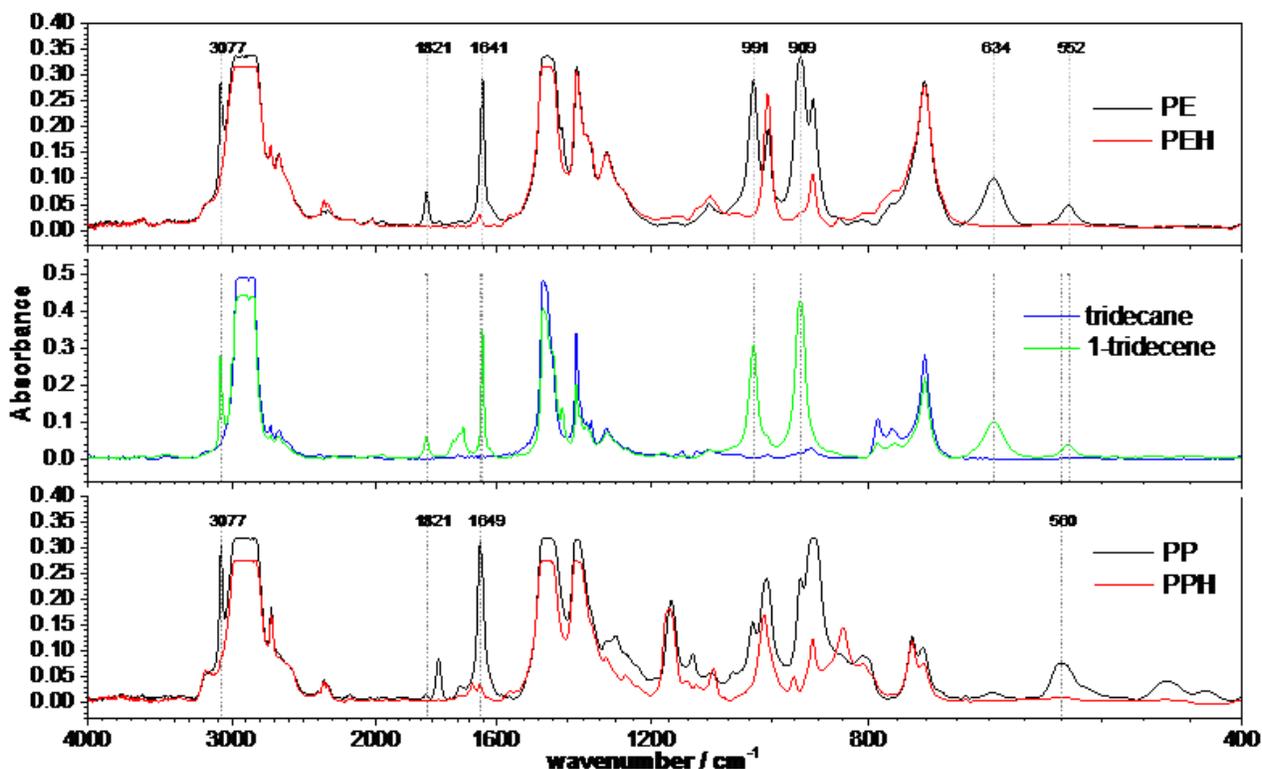
Figure 4. Comparison of samples before and after hydrogenation by IR-spectroscopy

In Tab. 4, the specified values of some of the prescribed performance characteristics of the samples before and after the hydrogenation are also given by the prescribed value. It is evident that, in addition to the density and sulfur content of the samples, they meet the standard values for diesel fuels. Samples have lower density values than the lower density limit specified in the standard. This is due to the minimum content of aromatics in these fractions and the high content of linear or branched alkanes and alkenes depending on the type of plastic. Lower density is typical for diesel fuels of alkanic character, and higher density is typical for more cyclical fuels, possibly fuels containing a higher proportion of aromatics. Lower density is positive for emission reductions, and polyalkenes hydrocarbon fractions could be a good ingredient in engine feeds. The sulfur content exceeds the standard value several times and does not change by hydrogenation. It has been shown that the catalyst used, and the reaction conditions used to saturate the unsaturated hydrocarbon bonds but did not cleave the molecules for the release of the sulfur compounds. It is important to highlight the good low-temperature properties of the hydrogenates, especially the PPH samples. Such a low limitation of filterability (-21°C) is achieved in the diesel fuel only after the addition of the depressant.

Table 4. Comparison of some selected sample properties before and after hydrogenation with normalized values for diesel fuels

Sample	PE	PEH	PP	PPH	Standard values	Standard
Density (15 °C), kg.m^{-3}	801	790	794	790	820 - 845	EN ISO 3675
Kinem. viscosity (40°C), mm^2.s^{-1}	2.27	2.35	2.76	2.89	2.00 – 4.50	EN ISO 3104
Water content, mg.kg^{-1}	52	34	42	24	max. 200	EN ISO 12937
Sulfur content, mg.kg^{-1}	100	130	147	129	max. 10.0	EN ISO 20884
Pour point, °C	-	2-0	-	*1	-	STN EN 23015
Cold filter plugging point, °C	-	-2	-	-21	0*2	EN 116

*1 – sample without mist, viscous, less transparent at -24 °C
*2 – standardized value for moderate climate, diesel Type B

4. Conclusion

PE and PP samples, and in particular PEH and PPH hydrogenates, are the diesel fuel ana-logues, so they should meet the prescribed engine fuel standard. Prospectively, the plastic recycling unit alone cannot prepare commercial automotive fuels for direct use. However, the aim is to prepare hydrocarbon fractions suitable for further processing in the refinery by using existing fuel production technologies by adding these fractions to refinery streams. Our results show that IR spectroscopy is a quick and reliable method for monitoring the degree of satu-ration for unsaturated bonds in hydrocarbon liquids from waste polyalkene recycling and this method gave good correlation with results obtained by gas chromatography.

Acknowledgement

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