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Quality Improvement of Middle Distillates from Thermal Decomposition of Waste Polypropylene

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The world-wide demand for engine fuels (in Europe the demand for diesel fuel) is continuously growing. Nowadays the amount of used bio-components is increasing, too. This increase is caused by the crude oil depletion, the environmental protection and the intent to reduce the energy dependency. The mainly used alternative component in diesel fuels is the biodiesel. The performance properties of biodiesel are less favourable (poor thermal and oxidation stability, lower energy content, unfavourable cold flow properties) than the fossil diesel fuels’ ones, so their blending can adversely affect the fuels properties. Thus is it important to develop and prepare another alternative fuels with better properties. A diesel fuel component with suitable properties can be obtained from waste polyolefin in several steps.

The objective of our quality improving experiments was to investigate the catalytic hydrogenation of the thermal decomposition products in 5, 10, 20 and 30 % blends with gas oil over transition metal catalyst. In the frame of this work the effect of the process parameters (temperature: 300 - 360 °C, pressure: 50 bar, liquid hourly space velocity: 1.0 - 3.0 h^{-1}, H_2/hydrocarbon ratio: 450 Nm^3/m^3) on the quality and quantity of the liquid products was investigated.

1. Introduction

The yearly world production of plastics in the past years was about 250 million tonnes and the corresponding amount in the European Union (EU) increased to 50 million tonnes (~20 % of the global consumption). Polyolefins (LDPE, LLDPE, HDPE and PP) are the main plastic materials and they account for 47 % of the total plastic demand. As an unavoidable result of this huge demand, the amount of post-consumer plastic waste generated in EU was also high: roughly 25 million tonnes. About 62 % of this waste is recovered and 38 % is disposed in landfills (Aguado et al., 2009). The energy recovery and mechanical or feedstocks recycling are useful options for the management of plastic wastes. Feedstock recycling of polyolefin plastic wastes has increased attention (Escola et al., 2011).

Nowadays the amount of used bio-components in the engine fuels is getting increased attention, too (Hancsók et al., 2013). The highest amount of the bio-derived fuels is produced from field-grown plants, for example from corn (bioethanol) or from rapeseed (biodiesel), which can cause significant greenhouse gas emission. The investigation of the impacts of the Indirect Land Use Change (ILUC) is on-going. One of the bio-component of diesel fuel with excellent performance properties is the bio gas oil (the mixture of iso- and n-paraffins) (Solymosi et al., 2014). This can be produced from bio-derived materials (vegetable oil, animal fat) and waste-derived materials (used cooking oil, waste animal fats, etc.), too (Hancsók et al., 2013). A diesel bending component with high quality can be also produced from waste polyolefins in several steps. The gas oil fraction generated in the first step by the thermal decomposition of polyolefins (Miskolczi et al., 2009) is not yet suitable for engine fuel purposes because of its high olefin content and thus it has inappropriate thermal and oxidation stabilities.

The thermal instability of the olefins is basically caused by the unsaturation of the hydrocarbon chains, so the number of the carbon-carbon double bonds. The extent of instability depends on the extent of unsaturation, so the presence of two or more double bonds in the hydrocarbon chain significantly decreases the stability.

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During the oxidative degradation free radicals are attacking the unsaturated bonds, depriving one hydrogen atom from the molecule. The oxidative mechanism occurring during degradation leads to the formation of oxidation products, which can influence the fuel properties, worsen the quality of fuels and the performance of the engines. Deposits can form during storage (Knothe et al., 2007). Therefore quality improvement is needed (Angyal et al., 2007), e.g. the saturation of olefins (Walendziewski et al., 2001), which can be performed alone or in mixtures with gas oils (Hamad et al., 2013). The fierce competition on the fuel market can require new developments and segmented marketing strategy. This segmentation needs new, special blending components in order to prepare specialty fuels having advanced properties like higher cetane, better fuel economy or environmentally friendly composition, etc., (Zöldy et al., 2013).

In our experimental work the quality improvement of blends of crude oil based and waste polyolefin originated, highly olefinic (> 30 %) gas oil fractions was investigated. The crude derived gas oil fraction had high sulphur and aromatic contents. Thus the aim of our work was not only the quality improvement of the plastic decomposition product with high olefin content (primarily the hydrogenation of the olefinic double bonds), but also the quality improvement of the crude derived gas oil components, in one catalytic step.

2. Experimental

The thermal cracking of waste polypropylene was carried out in laboratory scale continuously operating equipment at 550 °C temperature with 5 kg/h feed. The schematic diagram of the device can be seen on Figure 1. The feedstock was preheated and added into the reactor in molten state, where further melting and cracking of hydrocarbon chains occurred. The liquid products were separated into naphtha, gas oil and base oil boiling range fractions and residue fraction by distillation.

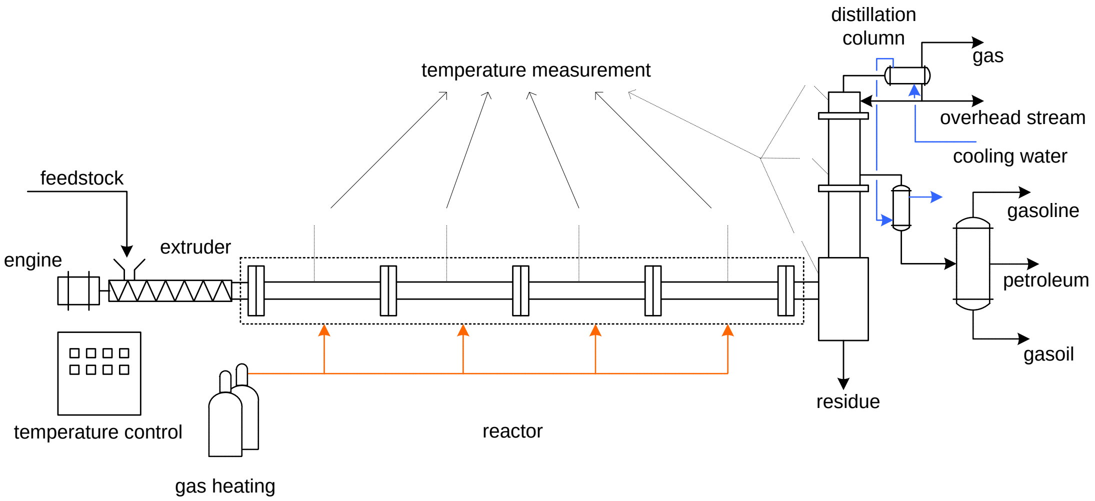

Figure 1: The schematic diagram of the device used for the thermal cracking of the waste polypropylene

The hydrogenation of the produced gasoil boiling range fractions was carried out in an equipment with a recirculation free, 100 cm^3 tubular reactor (Hancsók et al., 2012). It contained all the equipment and devices (pumps, separators, heat exchangers and controllers) applied in a reactor system of an industrial heterogeneous catalytic hydrogenation plant. The experiments were carried out in continuous operation, on a steady state catalyst. Commercial sulphided Ni(2.3 %)Mo(11.0 %)/Al_2O_3 catalyst was used in the experiments. The applied parameters were as follows: temperature: 320 - 360°C, pressure: 50 bar, liquid hourly space velocity: 2.0 - 3.0 h^{-1} and H_2/hydrocarbon ratio: 450 Nm^3/m^3 based on the preliminary experiments. The main properties of the used high-sulphur gas oil, thermal cracked gas oil fraction (PP cracked gas oil) and the 5, 10, 20, 30 % blends of these feeds are shown in Table 1.

The analytical and performance properties of the feedstocks and products were determined according to the standard analytical methods with the given precisions as shown in Table 2.

Table 1: The main properties of the used feedstocks

Main property	Straight run gasoil	PP cracked gasoil	PPGO AA5	PPGO AA10	PPGO AA20	PPGO AA30
PP crack gasoil content, %	0	100	5	10	20	30
Density, g/cm^3	0.8432	0.8037	0.8407	0.8390	0.8310	0.8295
Viscosity at 40 °C, mm^2/s	2.55	3.94	2.59	2.64	2.79	2.91
CFPP*, °C	-26	-21	-27	-26	-26	-27
Olefin content, %	<0.1	96.3	4.7	9.8	19.5	29.8
Aromatics content, w/w%	35.4	0.1	33.1	31.5	28.1	24.4
Polycyclic aromatic content, w/w%	12.5	0.0	11.8	11.3	10.1	8.7
Sulphur content, mg/kg	5472	12	4950	4681	3648	3554
Boiling range, °C						
Initial boiling point	164	203	164	161	169	166
Final boiling point	319	352	323	329	336	341

*Cold Filtering Plugging Point

Table 2: The used analytical methods

Properties	Analytical methods
Sulphur content	EN 20846:2012
Kinematic viscosity at 40 °C	EN ISO 3104:1996
Aromatic hydrocarbon content	EN 12916:2000
CFPP (cold filtering plugging point)	EN 116:1999
Density at 15,6 °C	EN ISO 12185:1998
Distillation characteristic	EN ISO 3405:2011
Olefin content	GC-MS: Shimadzu QP2010 Plus and Shimadzu QP2010 SE

3. Results and discussion

Based on the measured olefin content of the products the saturation of olefins was almost full with the application of any parameter combinations, the olefin concentrations of the formed products were below the detection limit (< 0.1 %).

The yield of the liquid products was above 96 % in every case. The yield of the liquid products obtained from the straight run gasoil with high sulphur content can be seen on Figure 2 as a function of the process parameters. The small amount of loss is caused by the sulphur removal and some cracking reactions. With the increase of the reaction temperature the efficiency of the sulphur removal reactions and the rate of cracking reactions increased, too, so the yield of the liquid products was lower. On Figure 3 the yield of the liquid products obtained from the PPGO AA 20 feedstock can be seen. The tendency was similar, but due to the lower sulphur concentration of the feeds and because of the olefin saturation the yield of liquid products was higher.

The Figure 4 demonstrates the density of the liquid products obtained from different feedstocks as a function of temperature in case of 3.0 h^{-1} liquid hourly space velocity. The density of the products was mainly affected by the composition of the feedstocks. However, the density of the products slightly decreased with increasing the temperature for the catalytic conversion of every feedstocks. The density of the product obtained from the PPGO AA 30 feedstock at 340 °C temperature was below the lower limit specified in the EN 590 standard. This is mainly caused by the catalysts higher activity at higher temperature, so the hydrogenation rate of the aromatic compounds has increased until 340 °C temperature. Above 340 °C the thermodynamic inhibition occurs, so the hydrogenation rate of the aromatic compounds was not higher and the densities were constant.

The densities of the products obtained from the PPGO AA 20 feedstock can be seen on Figure 5 as the function of the LHSV and the temperature. The lowest values appeared in case of 1.0 h^{-1} liquid hourly space velocity. This is caused by the longer residence time resulting greater hydrogenation and cracking reactions.

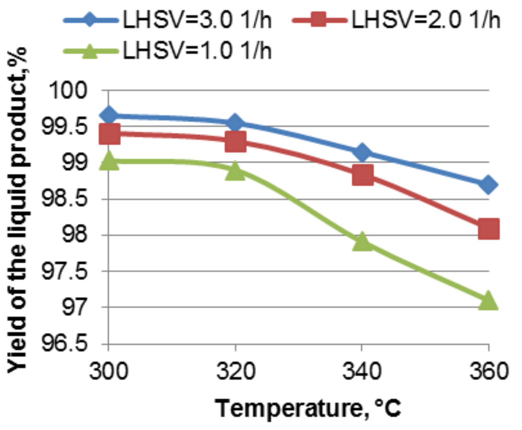

Figure 2: The yield of the liquid products as a function of the temperature and the LHSV, from the straight run gasoil (50 bar, 450 Nm^3/m^3)

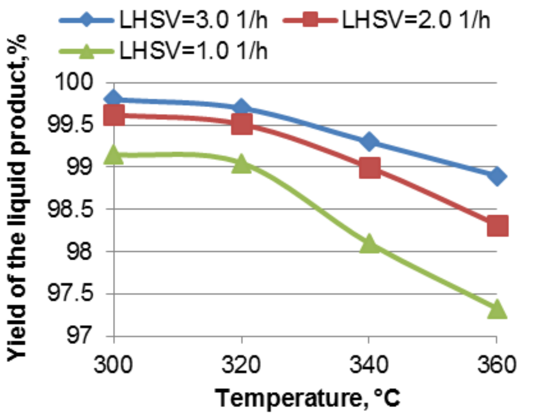

Figure 3: The yield of the liquid products obtained from the PPGO AA 20 feedstock as a function of the temperature and the LHSV (50 bar, 450 Nm^3/m^3)

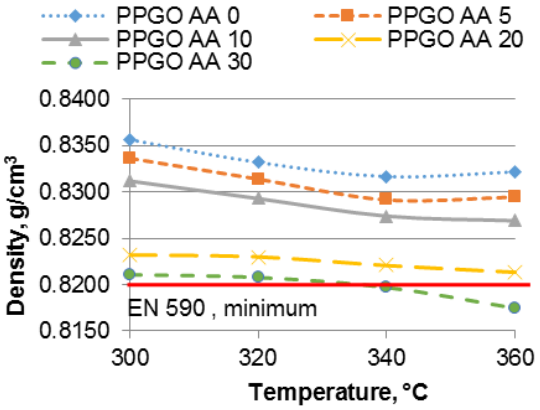

Figure 4: The density of the products as a function of the temperature and the feedstock (50 bar, 450 Nm^3/m^3,3.0 h^{-1})

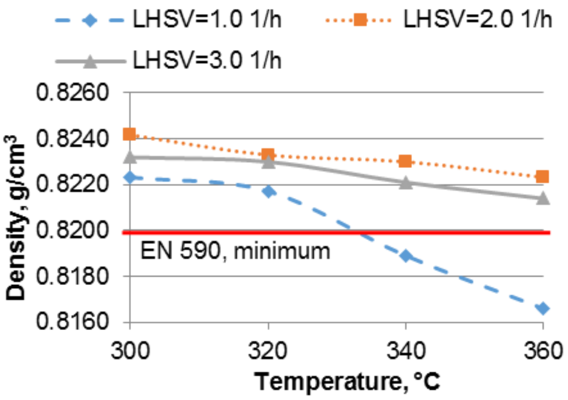

Figure 5: The density of the products obtained from the PPGO AA 20 feedstock as a function of the temperature and the LHSV (50 bar, 450 Nm^3/m^3)

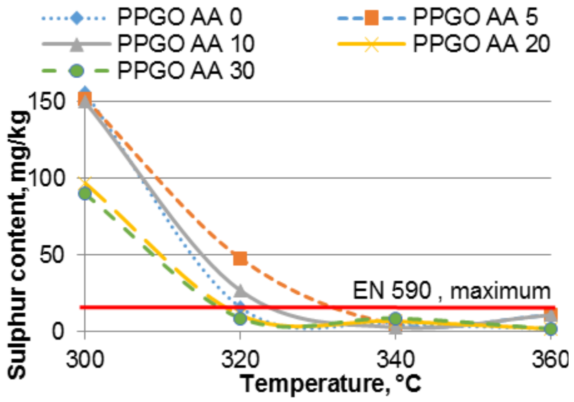

Figure 6: The sulphur content of the products as a function of the temperature and the feedstock (50 bar, 450 Nm^3/m^3,3.0 h^{-1})

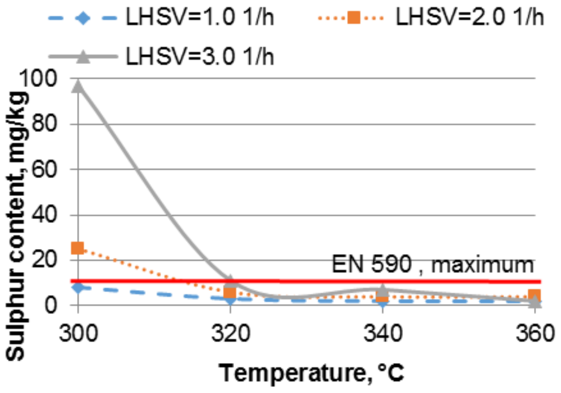

Figure 7: The sulphur content of the products obtained from the PPGO AA 20 feedstock as a function of the temperature and the LHSV (50 bar, 450 Nm^3/m^3)

The sulphur content of the products obtained from the different feedstock can be seen on Figure 6 as the function of temperature. With the higher PPGO content of the feedstocks the sulphur content of them decreased, so the sulphur content of the products decreased, too, by the same temperature and LHSV values. Figure 7 shows the sulphur contents of the products obtained from PPGO AA 20 feedstock as the function of temperature. The sulphur contents of the products obtained above 340 °C were below the upper limit specified in the diesel gasoil standard (maximum 10 mg/kg) in case of each feedstock. The activity of the catalyst was suitable at this temperature. The sulphur contents of the products obtained from the feedstocks with 10, 20 and 30 % PP cracked gas oil fraction were fulfilled the requirements already at 340 °C.

The cold filtering plugging point of the products changed between -23 and -28 °C, so they fulfilled the requirement of the winter quality diesel fuel standard (maximum -20 °C) in every case. As can be seen on Figure 8, the values of cold filtering plugging point slightly increased with the feedstocks higher PPGO content. This was because of the saturation of the olefins, which leads to the formation of n-paraffins with higher CFPP values.

The kinematic viscosity values were between 2.30 and 3.00 mm^2/s, they fulfil the limit range of the diesel gas oil standard in every case. The kinematic viscosity values of the products increased with the feedstocks higher PPGO content, too (Figure 9).

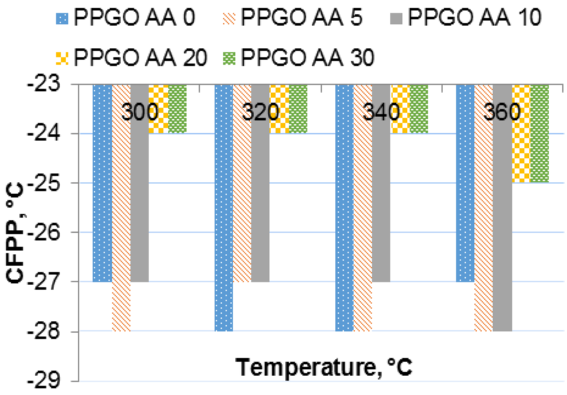

Figure 8. The cold filtering plugging point of the products as a function of the temperature and the feedstock (50 bar, 450 Nm^3/m^3,3.0 h^{-1})

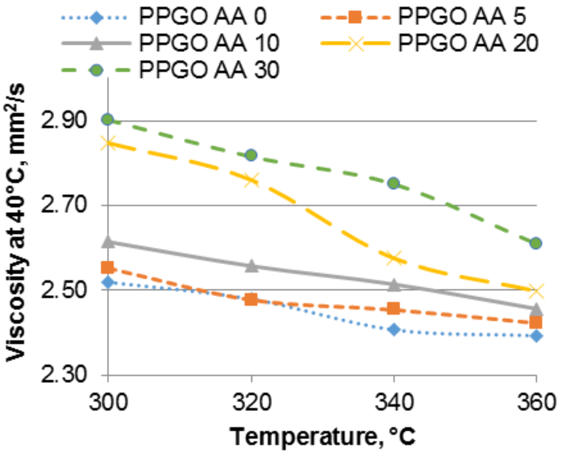

Figure 9. The kinematic viscosity of the products as a function of the temperature and the feedstock (50 bar, 450 Nm^3/m^3,3.0 h^{-1})

The aromatic contents of the products obtained from each feedstock decreased with the decrease of the LHSV because the rate of hydrogenation increased. This was caused by the longer residence time. With the increase of the temperature the aromatic content decreased until 340 °C. Above this temperature the aromatic content has not decreased further because of the thermodynamic inhibition. The inherently low aromatic content (0.1 %) of the cracked gas oil (PPGO) caused lower aromatic content of the products obtained from higher PPGO content feedstocks with inherently lower aromatic content. The polycyclic aromatic hydrocarbon content was below the upper limit specified in the diesel gasoil standard (maximum 8 w/w%) in case of each product.

4. Conclusions

The production of plastics has continuously grown in the past decades world-wide. In parallel to the plastic production the amount of plastic wastes has grown, too. From the plastic waste processing technologies the feedstock recycling seem to be a promising solution. A possible alternative diesel fuel blending component can be produced from waste plastics by thermal cracking. The resulted gas oil boiling range fraction cannot be directly used in diesel fuels because of its high olefin content, so its poor thermal and oxidation stability. Thus further quality improvement is needed. The co-processing with high-sulphur straight run gas oil can be a favourable solution.

In our experimental work the catalytic conversion of the high olefin content PP cracked gas oil (5, 10, 20 and 30 %) and straight run gas oil blends on a commercial sulphided NiMo/Al_2O_3 catalyst was investigated. Due to the qualitative characteristics of the products we determined that the blending of the cracked fraction hasn't adversely influenced the quality of the produced gas oil blending components. The saturation of the olefins was practically full; the olefin concentration of the products was below 0.1 %. During this quality improvement the paraffinic characteristic of the gas oil has increased because of aliphatic paraffin chains formed by the saturation of olefins and the heteroatom removal reactions. The formed products fulfil the specifications of the valid EU standard (EN 590:2013 Automotive fuels. Diesel. Requirements and test methods). In case of the application of the favourable process parameters (temperature: 340 °C, pressure: 50 bar, liquid hourly space velocity: 3.0 h^{-1}, H_2/hydrocarbon ratio: 450 Nm^3/m^3) the product with the best quality was obtained from the PPGO AA 30 feedstock. The sulphur content was 6 mg/kg, the aromatics content was 22.6 w/w% and the polycyclic aromatic content was 4.1 w/w% in this case. The density of this product was 0.8197 g/cm^3, so it was below the lower limit specified in the diesel gasoil standard (0.8200 g/cm^3). However, in a crude oil refinery the blending of this fraction with higher density stream is possible. The engine fuels are sold in volume, so the lower density leads to profit growth. Further investigation is needed to determinate the effect of higher blending ratios of the polypropylene cracking originated gas oil fractions and to determinate the process ability of other polyolefins thermal cracking originated fractions. In summary excellent gas oil blending component can be produced with the presented thermal and catalytic conversions.

Acknowledgments

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