Research Article

O. Tóth*, A. Holló, J. Hancsók

Catalytic quality improvement of waste polyolefin originated fractions

<https://doi.org/10.1515/cse-2018-0002>

Received September 29, 2017; accepted February 6, 2018

Abstract: The demand for alternative fuels having low greenhouse gases emission is continuously growing worldwide. Therefore it is preferred to produce new, waste originated components. One option is the recycling of plastic waste with cracking. The produced hydrocarbon fraction is not suitable for fuels thus it is important to improve its quality. The aim of our experimental work was to study the quality improvement of this cracked fraction (PPCGO) and crude oil based middle distillates (different composition) with co-processing. Our goal was to produce high quality diesel fuel blending components. We studied the effect of process parameters on the quality of products. Ni (2.3%) Mo (11.0%) P (2.3%)/Al₂O₃ catalyst was used. During the experiments we studied the hydrogenation of olefins, saturation of aromatics and desulphurization. The hydrogenation of olefins was practically complete at 300°C. It took place at significantly higher speed than the desulphurization reactions. In case of light gas oil feedstock the products had significantly lower sulphur contents; below 10 mg/kg already at 340°C. We determined that the cracked fraction had beneficial effect on the performance properties of the products. In case of all feedstock combinations, we found process parameters which can be used to produce high-quality diesel fuel blending components on the tested catalyst.

Keywords: alternative fuel, catalytic hydrogenation, olefin saturation, desulphurization, diesel fuel.

1 Introduction

The demand for biofuels among all fuels is continuously growing worldwide according to the BP database (www.bp.com/statisticalreview). At the same time the European Union limits the use of food-based biofuels to maximum 7% by 2020 and maximum 3.8% by 2030 in the Renewable Energy Directive (COM(2016) 767 final). This is the driving force to develop and produce other alternative fuels from waste and non-edible feedstocks.

The world-wide municipal solid waste generation is about 456 kg/person annually (www.worldbank.org). In the European Union together with industrial waste it is about 1755 kg/person annually of which 416 kg/person is landfilled (2015) (<http://ec.europa.eu/eurostat>). The amount of plastic waste per year is 34 kg/person, of which nearly 40% is deposited [1]. There are some recycling technologies for plastic waste utilization from which the thermal or catalytic cracking is suitable for producing hydrocarbons. This is currently happening about 1% of these wastes [2]. For producing hydrocarbons the appropriate possibility is the process of waste polyolefins. They have the largest quantity and they do not contain other elements than the carbon and hydrogen atom [3]. Another research field is the development and production of polymers that are easier to reuse or recycle [4]. Approximately 24% of the weight of plastic waste is polypropylene [5]. Therefore some research group investigated the thermal cracking of polypropylene waste in a few studies [6-8].

The thermal cracking of polyolefins leads to a wide range of products: gases, liquid hydrocarbon products, waxes and solid residues. The liquid products contain C₅-C₂₀ hydrocarbons; their molecular structure and yield depends on the properties of the applied catalyst and on the process parameters. Researchers primarily examine their use as fuels. The produced fraction has high olefin content (> 50-90%), so it is not suitable for fuel purposes and it is necessary to improve its quality [9]. About this field there is only few information in the literature [10,11].

*Corresponding author: O. Tóth, Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, Veszprém, 8200, Hungary, E-mail: totho@almos.uni-pannon.hu

A. Holló, J. Hancsók, Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, Veszprém, 8200, Hungary

The aim of our work was the quality improvement of the blends (5, 10, 20, 30%) of waste plastic cracked fraction and two different crude derived, straight-run gas oil (with high but different sulphur and aromatics content). We examined the production of high-quality diesel fuel blending components. We selected a commercial Ni (2.3%) Mo (11.0%) P (2.3%)/Al₂O₃ catalyst based on the results of our pre-selection experiments. We studied the effect of the process parameter combinations (temperature: 300–360 °C, liquid hourly space velocity: 3.0 h⁻¹, pressure: 50 bar, H₂/hydrocarbon ratio: 450 Nm³/m³) on the yields and quality of the liquid products. Based on the results we made findings about the hydrogenation of unstable olefins in the cracked fraction as well as about their effect on the performance of hydro-desulphurization and hydro-dearomatisation reactions. And we made findings about the effects of the quality features (e.g. sulphur and aromatic content) of the different gas oil fractions on the rate of olefin saturation.

2 Methods

We carried out the catalytic quality improvement of the gas oil blends in an equipment with a recirculation free, tubular reactor with 100 cm³ useful capacity. 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 [12]. We carried out the experiments in continuous operation, on a steady state catalyst. We ensured the

sulphide state of the catalyst by sulphur containing gas oil treatment. We adjusted the gas oils' sulphur content to 2.5% with dimethyl-disulphide. We separated the product mixture of the reactor into gas and liquid fractions in a separator. We separated the liquid fraction into gasoline and gas oil boiling range fractions by atmospheric distillation.

We prepared the feedstocks of the two different experiments with mixing one of the straight-run middle distillate fractions (light gas oil: LGO, heavy gas oil: HGO) and the highly olefinic cracked fraction (PPCGO) of waste plastic polypropylene in different rates (weight%). The main properties of the used feedstocks are shown in Table 1. The PPCGO contained nearly 87% isoolefin hydrocarbon that contribute to the low value of PPCGO's cold filter plugging point.

We determined the analytical and performance properties of the feedstocks and products according to the standard analytical methods (with the given tolerance) and GC-MS as shown in Table 2.

3 Results

The yield of gasoline fraction changed between 1 and 3% and increased with higher temperature due to the higher rate of cracking reactions. The share of gas products changed between 0.3 and 3.3% and also increased with higher temperature due the higher removal of sulphur- and nitrogen atoms. These heteroatoms left the system as H₂S and NH₃, respectively. In the following we only

Table 1. The main properties of the used gas oil fractions

Main properties	Polypropylene cracked gas oil (PPCGO)	Straight-run light gas oil (LGO)	Straight-run heavy gas oil (HGO)
Density, g/cm ³	0.8023	0.8432	0.8468
Viscosity at 40 °C, mm ² /s	3.71	2.55	2.89
CFPP*, °C	-16	-26	0
Olefin content, %	95.5	<0.1	<0.1
Total aromatic content, %	0.1	35.4	32.9
Polycyclic aromatic content, %	0.0	12.5	12.6
Sulphur content, mg/kg	7	5,472	6,770
Nitrogen content, mg/kg	11	4	228
Cetane index	67.3	47.7	49.9
Boiling range, °C			
Initial boiling point	211	164	180
Final boiling point	343	319	372

*Cold Filter Plugging Point

Table 2. Analytical methods for determine the properties of the feedstocks and products

Properties	Analytical methods
Density at 15.6 °C	EN ISO 12185:1998
Kinematic viscosity at 40 °C	EN ISO 3104:1996
CFPP (cold filter plugging point)	EN 116:1999
Olefin content	GC-MS: Shimadzu QP2010 Plus and Shimadzu QP2010 SE
Aromatic hydrocarbon content	EN 12916:2016
Sulphur content	EN 20846:2012
Sulphur compounds	2D-GC-PFD**
Cetane index	EN ISO 4264
Distillation characteristics	EN ISO 3405:2011

** Two-dimensional Gas Chromatography –Flame Photometric Detector

describe the characteristics of the target products, the diesel fuel (boiling point range: 180-360 °C).

Fig. 1 shows the gas oil (target product) yields obtained from the heterogeneous catalytic quality improvement of the two straight-run gas oil, the PPGO 20 and the TOAA 20 (20% polypropylene cracked fraction) feedstocks as the function of the temperature and the LHSV.

The rate of olefin saturation changed between 60% and 72% at 260 °C and 280 °C at 3.0 h⁻¹ LHSV. Interestingly, the olefin content of the products obtained by the same process parameters from feedstocks containing LGO and HGO was almost identical. It was below 0.1% in every case at 300 °C and above.

In Fig. 2 and Fig. 3 the sulphur content of the products obtained in case of the different feedstocks can be seen. Due to the low sulphur content of the cracked plastic waste the sulphur content of the feedstocks decreased in proportion with higher PPCGO content. Accordingly, the sulphur content of the products decreased as well. As we can see on the Fig. 2 and 3, the LGO products had significantly lower sulphur content; at 340 °C all of these values were below 10 mg/kg (EN 590: 2013 standard). While products from feedstocks containing heavy gas oil, achieved this limit only at 360°C.

Although the total aromatic content of light gas oil was slightly higher (35.4%) than the heavy gas oils' one (32.9%), their polycyclic aromatic content was almost identical (12.5 and 12.6%, respectively). At 300 °C products obtained from HGO containing feedstocks had lower total aromatic content. Above this temperature the products obtained from LGO containing feedstocks had lower aromatic content (Fig. 4). Higher PPCGO-containing

Fig. 1. The yields of the target products obtained from different feedstocks (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

Fig. 2. The sulphur content of the target products (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

feedstocks had inherently lower total aromatics content because the aromatic content of PPCGO was only 0.1%. The products obtained from feedstocks with higher PPCGO content had lower total aromatics contents than the products obtained from straight-run gas oils.

The polycyclic aromatic content of diesel fuels significantly contributes to the emission of pollutants from diesel vehicles, especially to particle emission. It is therefore important to study the changes in the concentration of these compounds in the products (Fig. 5).

In Fig. 6 we can see the changes in the density of target products. The density of the feedstocks had high effect on the product densities. Due to the PPCGO lower density, with increasing the PPCGO content the density of the feedstock and the products decreased, too. The density of the products was almost always within the limit values (0.820-0.845 g/cm³) of the European diesel standard (EN 590). At 360 °C in case of 30% PPCGO containing feedstock, this value was slightly below the lower limit (0.8120-0.8195 g/cm³).

The 95% (V/V) distillation temperature of the straight-run heavy gas oil was higher than 360 °C. Each product had lower value because the hydrogenation of polycyclic aromatics and heavy sulphuric compounds produced hydrocarbons with lower boiling points.

The changes of the density and distillation data determined the trends of the cetane index values. Increasing the reaction temperature did not have a significant effect on it. The quality of feedstocks, however, clearly influenced its value under the same technological conditions (Fig. 7).

The cold filter plugging point of the products produced from heavy gas oil containing feedstock changed between -2 and 0 °C, while the products derived from light gas oil containing materials changed between -28 and -24 °C.

The kinematic viscosity of the products varied between 2.30 and 3.24 mm²/s (EN590 standards: 2.00-4.50 mm²/s). Its value was mainly influenced by the kinematic viscosity of the feedstock.

4 Discussion

With increasing the temperature the rate of hydrogenation increased (reaction kinetic causes, catalyst activity and selectivity, increasing contact time on the catalytically active sites). The hydrogenating reactions took place on the catalysts' active sites, including the sulphur removal, the olefin and the aromatic hydrocarbon saturation reactions. Accordingly, the yield, sulphur content, total and polycyclic aromatic content and the density decreased

Fig. 3. The sulphur content of the target products (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

Fig. 4. The aromatics content of the target products (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

Fig. 5. The polycyclic aromatic content of the target products (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

while the cetane index increased. The reduction of the yield is caused by the losses occurring due to the desulphurization and cracking reactions. Based on the comparison of the yields of the products obtained under the same process conditions from the different feedstocks we determined that with the increase of the PPCGO content the yields increased as well. The reason is the inherently lower sulphur content of the feedstocks, thus the losses occurring during desulphurization were lower, too. As well as the cracked fraction of plastic waste used as feedstock blending component contains olefins whose hydrogenation has slightly increased the weight of the resulting liquid products. In addition, the hydrocracking reactions took place to a lesser extent. The reason for this is that due to the strong adsorption of olefins to the catalytically active sites, there is less available free site for other reactions.

The formation of products with significantly lower sulphur content from light gas oil containing feedstocks was not only the LGO's inherently lower sulphur content (5472 mg/kg) but the presence of more easily removable sulphur compounds (dibenzo-thiophenes < 1%). The HGO had inherently higher sulphur content (6770 mg/kg) and it contained more difficultly removable sulphur compounds (dibenzo-thiophenes > 20%). The olefin content of the feedstocks did not have significant effect on the sulphur removal reactions, the efficiency of sulphur removal did not decrease with the increase of the olefin content. Due to the low sulphur content of the cracked plastic waste (7 mg/kg) with higher PPCGO content the sulphur content of the feedstocks decreased. Accordingly, the sulphur content of the products decreased, too, on the same temperature values. The desulphurization efficiency changed between 65.7 and 99.98% in case of HGO and between 96.9 and 99.98% in case of LGO and increased with the tightening of process parameters. Based on these results, we found that the hydrogenation of olefins took place at a significantly higher rate than the desulphurization in the studied catalytic system. We also found that the quality of the gas oils in the feedstock blends had no effect on the saturation of olefins.

The total aromatics contents of the products decreased with the increase of the temperature using each feedstock until 360 °C. This result is the outcome of the increasing rate of hydrogenation (kinetic effect) [13]. The highest value of the aromatics saturation efficiency was 33.70% in case of HGO and 54.3% in case of LGO and also increased with the tightening of the process parameters. This is because the aromatic compounds in the light gas oil can hydrogenate more easily, so the rate of aromatic saturation is higher. The olefin content of the feedstocks had no significant effect on the aromatic saturation reactions.

Fig. 6. The density of the target products (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

Fig. 7. The cetane index of the target products (50 bar, 450 Nm³/m³, 3.0 h⁻¹)

There was a significant reduction in the polycyclic aromatic hydrocarbons content even on 300 °C and it increased with increasing the temperature. On 340 °C and above the polycyclic aromatic hydrocarbons content has not decreased further significantly because of the thermodynamic inhibition [14]. It can be explained by the exothermic reactions of the saturation of polycyclic aromatic hydrocarbons. In the products obtained from heavy gas oil containing feedstocks, the higher polycyclic aromatic content was caused by the presenting dibenzo-thiophene derivatives which are more difficult to hydrogenate. The polycyclic aromatic saturation efficiency changed between 46.2 and 92.6%, in case of HGO and between 82.0% and 99.3% in case of LGO. The polycyclic aromatic hydrocarbon content of each product was between 0 and 7% (maximum 8% in the EN 590 European diesel fuel standard).

With increasing the temperature, the density of the targeted products has decreased. The reason for this is the increasing rate of olefin and aromatic hydrogenation. The density is also reduced by sulphur removal. Due to the higher hydrogen content of the molecules, the density decreased. The products obtained from the lower density LGO feedstocks had lower density respectively. The lower density product can be blended with other high density diesel fuel blending components which can have lower economic value. In addition, the fuels are sold in volume and therefore the use of components with lower density but otherwise suitable properties may lead to significant profit growth.

The cetane index of the products obtained from LGO containing feedstocks was lower than those obtained from HGO containing ones. Although the decrease of density also increases the cetane index, the cetane index increasing effect of the increase in the average boiling point is relatively higher. With higher PPCGO content the cetane index of the products increased. This is caused by the increase of produced paraffin hydrocarbons from the hydrogenation of olefins. With this the density decreases and the boiling point range shifts.

Due to their cold filtering plugging point values the HGO containing products are suitable for blending component of summer-grade, the LGO containing products for winter-grade or arctic diesel fuel.

The kinematic viscosity of the products slightly decreased with increasing the temperature. This is the result of olefin saturation, sulphur removal and aromatic hydrogenation.

The products formed at 360 °C fulfil the specifications of the valid EU standard in case of each feedstock (EN 590:2013 Automotive fuels. Diesel. Requirements and test methods).

In summary excellent gas oil blending component having high hydrogen content in the molecule can be produced with the presented catalytic conversion of the feedstocks. The co-processing with high-sulphur straight-run gas oil can be a favourable solution to improve the quality of waste polypropylene thermal cracked gas oil fractions. We found that the blending of waste based fraction into the feedstock had beneficial effect on the qualitative characteristics of the products (e.g. higher cetane index due to the higher content of saturated hydrocarbons, so that the products obtained from light gas oil can be sold as a high-energy diesel fuel suitable for premium quality or even arctic requirements applying appropriate additives). During the quality improving step aliphatic paraffin chains formed and the paraffinic characteristic of the products increased.

For each feedstock, we found such process parameter combinations that can be used to produce high quality diesel fuel blending components on the tested catalyst.

Acknowledgements: The authors acknowledge the financial support of the project of the Economic Development and Innovation Operative Programme of Hungary, GINOP-2.3.2-15-2016-00053: Development of liquid fuels having high hydrogen content in the molecule (contribution to sustainable mobility) and the project of Széchenyi 2020 under the EFOP-3.6.1-16-2016-00015: University of Pannonia's comprehensive institutional development program to promote Smart Specialization Strategy. The Project is supported by the European Union and co-financed by Széchenyi 2020. The authors acknowledge the GCxGC MS analysis of Refinery R&D Lab of MOL Plc.

Abbreviations

PPCGO – polypropylene cracked gas oil
LGO – straight-run light gas oil
HGO – straight-run heavy gas oil
LHSV – liquid hourly space velocity
PPGO 20 – 20% PPCGO containing light gas oil
TOAA 20 – 20% PPCGO containing heavy gas oil

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