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Production of Diesel Fuel with Alternative Components Content from Various Wastes

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The use of renewable energy sources is continuously growing worldwide. The demand for alternative fuel components from renewable sources in Europe is also increasing. To ensure economically sustainable transport and shipping, it is inevitable that the production of alternative fuels from waste sources will be increased. The aim of this research work was to produce high quality, alternative components containing diesel fuel and to study the hydrogenation and the interaction among the different compounds of the waste polyolefin cracking fraction (10 %), waste fatty acid fraction (10, 20 and 30 %) and the high sulphur gas oil. The catalytic conversion of the mixtures was carried out on a commercial, sulphided $NiMo/Al_2O_3P$ catalyst. High-quality diesel fuel component with high hydrogen content (13.65 %), high cetane number (57.0) and reduced expected emissions was produced under the favourable process parameters (temperature: 360 °C, hydrogen/hydrocarbon volume ratio: 600 Nm^3/m^3, pressure: 50 bar, and liquid hourly space velocity: 1.0 h^{-1}). The obtained product is more environmentally friendly than conventional diesel fuels and can contribute to reduce the amount of landfilled wastes.

1. Introduction

In the European Union (EU) the consumption of gas oil/diesel fuel is more than 200 million tonnes/year, from which 3.5 e % should be advanced biocomponent by 2030 (EU, 2018). The amount of landfilled plastic wastes is nearly 7.5 million t/year (Plastics, 2017) and the amount of waste fatty acids generated during the production of vegetable oil is circa 0.3 – 0.6 million t/year in the EU (OECD, 2017). These wastes could be promising feedstocks for diesel fuel component production.

Hydrocarbons can be produced from waste plastics by chemical recycling (Lopez et al., 2017). Figva and Dimitriou (2017) found that the chemical recycling plant of polymers can be operated economically with at least 1000 kg/h capacity. Within this process, the recycling possibilities of waste polyolefins should be considered since these are generated in the largest quantities and they mainly contain no other elements than carbon and hydrogen (Buekens et al., 2000). The middle distillate products formed during special thermal cracking of polymers contain C_{13}-C_{21} hydrocarbons, mainly olefins. These products are proposed to be fuel blending components (Kalargaris et al., 2017) even though they do not meet the requirements of the EU and international standards. So they can only be used as engine fuels when their quality is improved (Bezergianni et al, 2017). The co-hydrogenation with unrefined gas oils is a good solution for improving the quality of the cracked fraction of waste plastics (Tóth et al., 2018).

Fatty acids can be produced from various sources (Srivastava and Hancsók, 2014). A by-product of the paper industry is tall oil and it contains 97% fatty acids (Kocík et al., 2017). Fatty acids can be used to produce biodiesels (Sierra-Cantor and Guerrero-Fajardo, 2017). Hydrocarbons can also be produced from waste fatty acids during deoxygenation (Hermida et al., 2015) so they are promising alternative feedstocks of engine fuels (Santillan-Jimenez et al., 2013). The deoxygenation of fatty acids with in-situ hydrogen production from water is not yet suitable for industrial scale use (Zhong et al., 2019). The hydrogenation of pure fatty acids can lead to corrosion problems in the hydrogenation units, but the co-processing with straight run gas oil is a potential solution (Sági et al., 2017). Sulphided $NiMo/Al_2O_3P$ catalyst can be used for the co-processing of fatty acid mixtures and gas oil fractions (Visnyei et al., 2018).

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The blending of the waste polypropylene cracked fraction to high sulphur gas oil has practically no effect on the desulphurisation efficiency (Tóth et al., 2018). Meanwhile the blending of the waste fatty acid fraction is less favourable during the co-processing with unrefined gas oils (Tóth et al., 2019). There is no available information in the literature about the co-hydrogenation of high sulphur gas oils with both waste components. Therefore, the interaction of the different compounds of the two alternative components and their conversion in gas oil mixtures need to be studied.

2. Experimental

2.1 Catalytic tests

A catalytic system containing a tubular reactor (100 cm^3 effective volume) without back-mixing was used for the hydrogenation of the feedstocks (Hancsók et al., 2007) in continuous mode. The experiments were conducted on a sulphided, steady-state NiMo/Al_2O_3-P catalyst. The catalyst selection was based on preliminary experiments. The effect of the process parameters (temperatures of 300 – 360 °C, hydrogen/hydrocarbon volume ratio of 600 Nm^3/m^3, pressure of 50 bar, and liquid hourly space velocity of 1.0 – 3.0 h^{-1}) on the quality and quantity of the main products has been studied. The main products (gas oil fractions: 180 °C – 360 °C) obtained by distillation of the liquid product mixtures.

2.2 Materials

Table 1 summarizes the main properties of the used unrefined heavy gas oil (HGO), polypropylene cracking fraction (PPCF), waste with high fatty acid content (WHFA) and the feedstock blends with 10 wt % PPCF and 10, 20 and 30 wt % WHFA content. The PPCF was produced by thermal cracking of industrial polypropylene waste in a continuously operating laboratory scale equipment at 550 °C temperature and 5 kg/h feed. The WHFA was formed during vegetable oil production.

Table 1: Main properties of the feedstocks and feedstock blends

Main property	HGO	PPCF	WHFA	HPF-0	HPF-1	HPF-2	HPF-3
Waste fatty acid fraction content, wt %	-	-	100	-	10	20	30
Polypropylene cracking fraction content, wt %	-	100	-	10	10	10	10
Sulphur content, mg/kg	7,396	7	13	6,201	5,809	4,993	4,251
Total aromatic content, wt %	32.9	0.0	0.0	29.1	27.6	24.8	21.6
PAH* content, wt %	12.6	0.0	0.0	11.1	9.9	8.9	7.5
Hydrogen content, wt %	13.07	14.10	11.46		12.91	12.81	12.61
CFPP**, °C	0	-16	20	-1	-1	-1	1

*Polycyclic Aromatic Hydrocarbon **Cold Filter Plugging Point,

2.3 Analytical methods

Table 2. summarizes the analytical methods applied for determining the properties of the feedstocks and products.

Table 2: The used analytical methods

Properties	Analytical methods
Hydrocarbon composition	GC method, Shimadzu GC 2010
Sulphur content	EN ISO 20846:2012
Aromatic hydrocarbon content	EN 12916:2016
Hydrogen content	ASTM D7171-05
Density at 15.6 °C	EN ISO 12185:1998
Kinematic viscosity at 40 °C	EN ISO 3104:1996
Cold Filter Plugging Point	EN 116:2016

3. Results and discussion

3.1 Yield of the main products

The yield of the main products (boiling range: 180 °C – 360 °C) decreased with increasing the temperature and the WHFA content of the feedstocks as it can be seen on Figure 1 at 2.0 h^{-1}. The yield decreasing effect of the WHFA fraction is caused by the oxygen removal reactions. During these reactions H_2O, CO and CO_2 by-products are formed. The hydrogenation of PPCF with high olefin content led to yield growth. With increasing the temperature, the rate of heteroatom removal reactions of HGO fraction is increasing, so the amount of obtaining H_2S and NH_3 products increased, too. Due to these effects, the yield of the main products was lower than the yield from hydrogenation of only PPCF containing feedstocks.

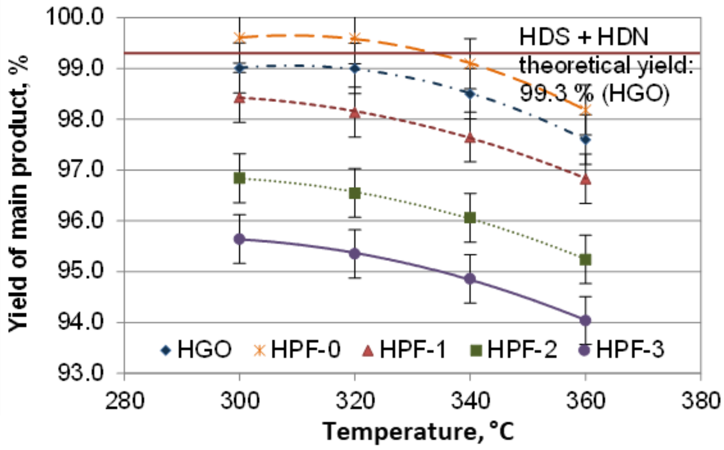

Figure 1: Yields of the main products obtained from the different feedstocks as a function of temperature (LHSV: 2.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

The saturation of olefins and the removal of oxygen atoms were full in all cases based on the iodine-bromine numbers and gas chromatography analysis of the main products.

3.2 Most important characteristics of the main products

The sulphur content of the main products decreased with the increasing of alternative component ratio in the feedstocks (Figure 2). This is caused by the lower sulphur content of the feedstocks due to the inherently low sulphur content of the alternative components (PPCF: 7 mg/kg, WHFA: 13 mg/kg). The effect of the temperature rise was positive on the hydrodesulphurisation reactions because the activity of the catalyst and the rate of these reactions increased. The sulphur removal efficiencies were also higher with increasing the temperature. With the increasing WHFA content of the feedstock the sulphur removal efficiency decreased. Main products with lowest sulphur content obtained from the only PPCF containing feedstock (HPF-0). The main products obtained at 360 °C and 1.0 h^{-1} meet the requirement of the EN 590:2017 diesel fuel standard (≤ 10 mg/kg) except the main product from the HPF-3 feedstock.

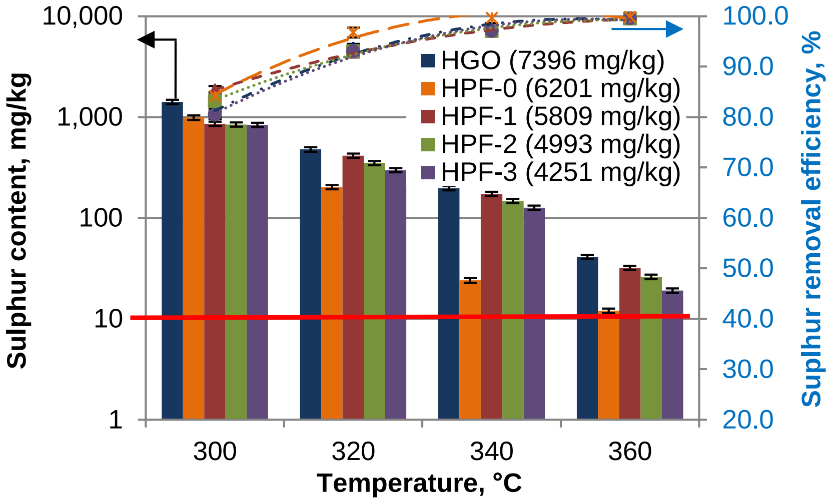

Figure 2: Sulphur content of the main products obtained from the different feedstocks as a function of temperature (LHSV: 2.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

The total aromatic content of the main products decreased with increasing the temperature because of the increasing hydrodearomatization reaction rate. Since the PPCF and WHFA were practically aromatic free, increasing the rate of these fractions decreased the total aromatic and polycyclic aromatic content of the feedstock blends. The total aromatic and polycyclic aromatic content of the main products decreased with increasing the alternative component content but not proportionally. The efficiency of the aromatic saturation reactions decreased with higher alternative component content due to the higher number of competitive reactions on the catalysts active sites and lower amount of excess hydrogen. The polycyclic aromatic contents of the main products had a minimum value at 340 °C (Figure 3). Above this temperature the PAH content increases because the saturation of these compounds is highly exothermic.

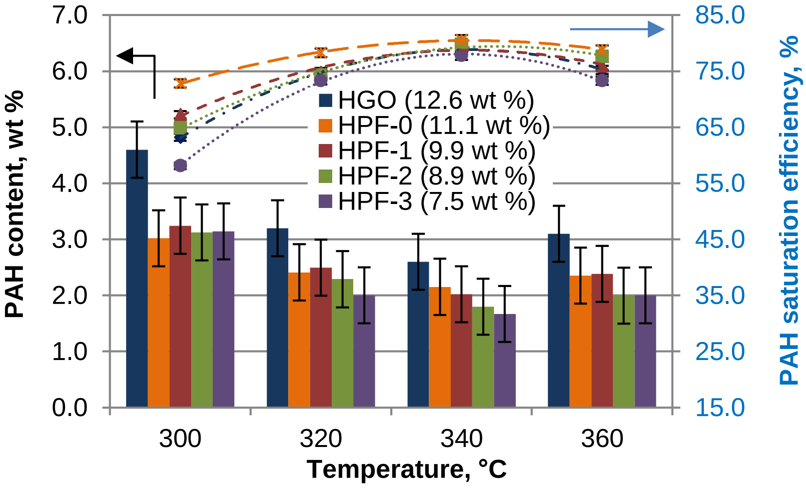

Figure 3: Polycyclic Aromatic Hydrocarbon content of the main products obtained from the different feedstocks as a function of temperature (LHSV: 2.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

The hydrogen content of the main products increased with the increasing ratio of sulphur, nitrogen, oxygen removal and olefin, aromatic saturation reactions. Since the saturation of olefins and the removal of oxygen atoms were full in every case the effect of these reactions was constant by changing the temperature. With the hydrogenation of the PPCF C_{13}-C_{21} isoparaffins, with the hydrogenation of the WHFA C_{17}-C_{18} normal-paraffins were formed. These compounds have high hydrogen content in their molecular structures. So the increasing amount of alternative components in the feedstock blends leads to higher hydrogen content. The slight decrease in the hydrogen content at 360 °C is caused by the increasing PAH content of the main products (Figure 4).

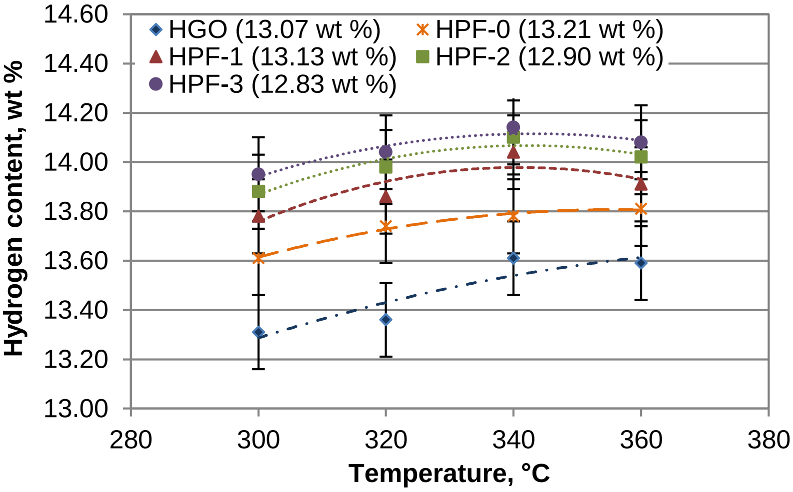

Figure 4: Hydrogen content of the main products obtained from the different feedstocks as a function of temperature (LHSV: 2.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

3.3 Other properties of the main products

The effect of the feedstock blends composition and the process parameters on the performance properties of the main products was also investigated. With increasing WHFA content of the feedstock blends the density of the feedstock blends increased while the density of the obtained main products decreased. This is caused by the lower density of formed n-paraffins. The density of the main products decreased with increasing temperature and residence time and it met the requirement of the EN 590:2017 diesel fuel standard in each case. The kinematic viscosity of the main products was mainly affected by the composition of the feedstock blends, it increased with increasing the ratio of alternative feedstock. It slightly decreased with the increasing of the temperature and the residence time and it met the requirements of the standard in case of each main product. The cetane index of the main products also increased with increasing the blending ratio of the alternative feedstocks. It is caused by the increasing ratio of formed i-paraffins and n-paraffins in the main products which reduces density and increases the mean average boiling point. The temperature and the liquid hourly space velocity had no significant effect on this property. The composition of the feedstock blends had significant effect on the cold filter plugging points of the main products while the temperature and the liquid hourly space velocity did not (Figure 5). With increasing the WHFA content of the feedstock blends the cold filter plugging points of the main products increased, too due the formed C_{17}, C_{18} n-paraffins. Besides this the C_{13}-C_{21} i-paraffins formed from the PPCF reduced the cold filter plugging points of the main products compared to the conventional HGO fraction. The main products obtained from HPF-3 feedstock did not meet the cold flow property requirements of the summer-grade diesel fuel of the standard.

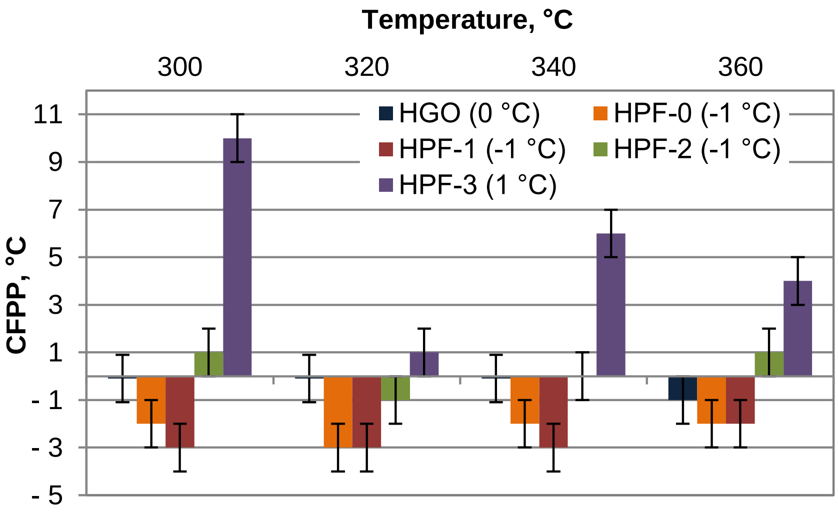

Figure 5: CFPP of the main products obtained from the different feedstocks as a function of temperature (LHSV: 2.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

4. Conclusions

Based on the result of the experiments (catalyst: commercial NiMo/Al_2O_3P; temperature: 300 – 360°C; hydrogen/hydrocarbon ratio: 600 Nm^3/m^3; pressure: 50 bar; liquid hourly space velocity: 1.0 – 3.0 h^{-1}) favourable operation parameters to produce high quality diesel fuel blending components (e.g. 10 wt % fatty acid waste and 10 wt % waste polypropylene cracked fraction containing feedstock, temperature: 360°C, liquid hourly space velocity: 1.0 h^{-1}) were selected. Based on the availability on the waste fatty acids and the consumed diesel fuel, all waste fatty acid formed in the EU could be used as alternative diesel fuel component. It would be 0.27 e % advanced biocomponent considering the weight loss of the feed during deoxygenation and that, the energy content of the co-processed oil of biomass is equal to the fossil diesels energy content. The amount of formed middle distillate during thermal cracking of polyolefins is estimated to be 10 wt %. It would mean 0.75 million t/year if landfilled plastic wastes would be chemically recycled. This is another 0.38 e %. Together it would be 0.65 e % but waste sources counted as double. So it would be 1.3 e % which can be further increased since lots of plastic waste has been deposited in nature already. This garbage should be treated soon since it has already got into the food chain. Overall high quality diesel fuel blending component with high hydrogen, low sulphur and aromatic content and high cetane index, so with lower expected emissions can be produced with the presented catalytic conversion. The effect of the blending of only the waste polypropylene cracking fraction into the unrefined feedstock on the quality and quantity of the main products was the most favourable. The waste fatty acid fraction had an unfavourable effect compared to the waste polypropylene cracking fraction.

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References

Bezergianni S., Dimitriadis A., Faussone G-C., Karonis D., 2017, Alternative Diesel from Waste Plastics, Energies, 10, 1750, 1–12.

Buekens A.G., De Caevel B., De Vos M., 2000, Waste Plastics as a Source of Petrochemical Base Materials, Petrochemical Processes, 1, 91-98.

European Parliament and Council, 2018, Brussels, Directive of the European Parliament and of the council on the promotion of the use of energy from renewable sources (recast) COM (2016) 767 final/2 2016/0382 (COD) (November 21, 2018)

Figva A., Dimitriou I., 2018, Pyrolysis of plastic waste for production of heavy fuel substitute: A techno-economic assessment, Energy, 149, 865–874.

Hancsók J., Magyar Sz., Szoboszlai Zs., Kalló D., 2007, Investigation of energy and feedstock saving production of gasoline blending components free of benzene, Fuel Processing Technology, 88(4), 393-399.

Hermida L., Abdullah A.Z., Mohamed A.R., 2015, Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism, Renewable and Sustainable Energy Reviews, 42, 1223–1233.

Kalargaris I., Tian G., Gu S., 2017, The utilisation of oils produces from plastic waste at different pyrolysis temperature in a DI diesel engine, Energy, 131, 179-185.

Kocík J., Samikannu A., Bourajoini H., Pham T.N., Mikkola J-P., Hájek M., Capek L., 2017, Screening of active solid catalysts for esterification of tall oil fatty acids with methanol, Journal of Cleaner Production, 155, 34–38.

Lopez G., Artetxe M., Amutio M., Bilbao J., Olazar M., 2017, Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review, Renewable and Sustainable Energy Reviews, 73, 346–368.

OECD, 2017, OECD-FAO Agricultural Outlook 2017-2026

Plastics – the Facts 2017, 2017, An analysis of European plastics production, demand ad waste data

Santillan-Jimenez E., Morgan T., Lacny J., Mohapatra S., Crocker M., 2013, Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel, Fuel, 103, 1010–1017.

Sági D., Holló A., Varga G., Hancsók J., 2017, Co-hydrogenation of fatty acid by-products and different gas oil fractions, Journal of Cleaner Production, 161, 1352–1359.

Sierra-Cantor J.F., Guerrero-Fajardo C.A., 2017, Methods for improving the cold flow properties of biodiesel with high saturated fatty acids content: A review, Renewable and Sustainable Energy Reviews, 72, 774–790.

Srivastava S.P., Hancsók J., 2014, Fuels and Fuel-Additives, John Wiley & Sons, Inc., Hoboken, New Jersey

Tóth O., Holló A., Hancsók J., 2018, Catalytic quality improvement of waste polyolefin originated fractions, Catalysis for Sustainable Energy, 5, 12-18.

Tóth O., Holló A., Hancsók J., 2019, Co-processing a waste fatty acid mixture and unrefined gas oil to produce renewable diesel fuel-blending components, Energy Conversion and Management, 185, 304-312.

Visnyei O., Sági D., Holló A., Auer R., Hancsók J., 2018, Long-Term Performance of NiMo/Al_2O_3 Catalyst during the Co-processing of Fatty Acid By-Products and Gas Oil Fraction, Chemical Engineering Transactions, 70, 727-732.

Zhong H., Jiang C., Zhong X., Wang J., Jin B., Yao B., Luo L., Jin F., 2019, Non-precious metal catalyst, highly efficient deoxygenation of fatty acids to alkanes with in situ hydrogen from water, Journal of Cleaner Production, 209, 1228-1234.