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Feedstocks for Engine Fuels from Waste Polyolefins

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Hydrogenation and hydroisomerization of kerosene fractions produced by thermal cracking of polyethylene, polypropylene and those mixtures were studied on Pt/SAPO-11 catalyst. Effects of the process parameters and the composition of the feedstocks on the isoparaffin contents, and the main performance properties of JET fuels (e.g. freezing point, smoke point) were examined. It was found that, practically sulphur- olefin- and aromatic free kerosene fractions having excellent burning properties (smoke point: 42.0 – 50. 0 mm) can be produced from the tested polyolefin cracked fractions. In the examined catalytic system JET fuel with adequate freezing point can only be produced from the clear cracked fraction of polypropylene. Due to the inadequate freezing point and density the products of the experiments cannot be used directly as engine fuel, just only as high value blending components.

1. Introduction

The total production of plastics was reached about 335 Mt in 2016 (Lopez et al., 2017). Due to the excellent properties of plastics such as durability, flexibility and cheapness their application was gradually increased over the past 50 years (Saleem et al., 2018). Nowadays, plastics play a vital role in everyday life of human (Owusu et al., 2018). Economic growth, development of the packaging and construction industries and change of consumers' behaviour resulted rapid increase in plastic waste generation. Currently, plastics are about 7 – 10 % of municipal solid waste (Glushkov et al., 2018). Based on the foregoing their share in MSW will be 9 – 13 % in 2025 (Hoornweg et al., 2012). Plastics are unable to degrade within a reasonable time. Landfills cause serious problems because of the environmental load. In order to minimize the amount of landfilled plastic incineration and mechanical recycling are the most commonly applied techniques (Serrano et al., 2012). During incineration dioxin and furan derivatives can be emitted into the atmosphere and mechanical recycling is economical only when selectively collected high purity waste is available (Miskolczi et al., 2009). In this process mechanical properties of plastics may also be deteriorate. Chemical recycling is a well-established route to manage plastic waste. Cracking has gained increasing interest worldwide (Miandad et al., 2017). Liquid products obtained in polyolefin cracking contains olefin hydrocarbons in significant amount, therefore cannot be used straightforward as engine fuel. Olefins result formation of resins in the engines during the storage (Kriván et al., 2016). Nonetheless, limited information is available about their quality improvement in the literature (Escola et al., 2012). In most cases, the quality improvement of cracked fractions was attempted with modifying the process parameters of the chemical recycling (Gulab et al., 2010) or using catalysts (Kaminsky and Zorriqueta, 2007). Catalysts decrease the energy demand of cracking and shift the product formation towards smaller molecular weight fractions. Due to contaminants and high viscosity residues they can loss rapidly their activity (Uemichi et al., 1998). The necessity of using of catalyst in the first step of polyolefin cracking had also questioned by Venkatesh et al., (1995). Marcilla et al., (2004) have similar conclusions, too. The quality improvement of polyolefin cracked fractions was also carried out by Escola et al., (2017) after removal of high viscosity residues and contaminants. The quality improvement of kerosene fraction of cracking was only investigated by few research groups (Zhang et al., 2017). They produced aliphatic alkenes and aromatic hydrocarbons on ZSM-5 catalyst by applying microwave induced degradation of low density polyethylene (Zhang et al., 2016). The first step was followed by the hydrogenation of the unsaturated hydrocarbons on Raney nickel catalyst (T = 150 –

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250 °C). The optimal process parameters were the following 250 °C, 35 bar, 2 h, 5 % Raney nickel catalyst for the production of JET fuel with improved quality. The concentration of aliphatic alkanes, cycloalkanes and aromatic hydrocarbons was 32.2 %, 53.1 % and 15.0 % in the JET fuel at these process parameters. The specification of hydrotreated product was equal to those of JP-5 fuel. Due to the high pour point of n-olefin and n-paraffin hydrocarbons JET fuel with adequate freezing point cannot be produced from the mixtures of 10 – 30 % polyethylene cracked fraction and 90 – 70 % straight-run kerosene by hydrogenation (Tomasek et al., 2017). Additionally, the freezing points of hydrotreated polypropylene (PP) and polyethylene (PE) cracked fractions are also higher than -47 °C. These results clearly show that hydroisomerization of the polyolefin crack products is needed to improve their cold flow properties. Its possibility has not been investigated in the literature, especially in production of JET fuels, in continuous operation mode. Currently, the issue of the usage of the resulting products hinders the spread of the chemical recycling. Involving the crack products in the production of engine fuels is a remaining task to be solved.

2. Experimental part

The aim of the experimental work was to produce isoparaffin rich JET fuels by hydrogenation and hydroisomerization of kerosene boiling point fraction of waste polypropylene and polyethylene thermal cracking products. Experiments were carried out on Pt/SAPO-11 catalyst in the temperature range of 320 – 360 °C, at pressure of 40 bar, hydrogen to hydrocarbon ratio of 400 Nm^3/m^3 and by liquid hourly space velocity (LHSV) 1.0 and 2.0 h^{-1}. Effects of the feedstock composition and the process parameters on the yields and the freezing- and smoke points of the liquid products were examined. The aim of the experiments carried out with feedstock mixtures (10 – 50 % of polyethylene and 90 – 50 % of polypropylene content) was to model the composition of different polyolefin wastes.

2.1 Feedstock preparation

Cracking of polyethylene (PE100), polypropylene (PP100) and feedstock mixtures (10PE90PP, 20PE80PP, 30PE70PP, 50PE50PP) was carried out in continuous reactor (Tóth et al., 2016) with a feed rate of 4 kg/h at 550 °C. The liquid product of cracking was separated by distillation to gasoline, kerosene and gasoil fractions. The kerosene boiling point fractions did not contain sulphur compounds and aromatic hydrocarbons. Due to the lack of aromatics their smoke points were much higher than the required 25 mm (Table 1). Since the smoke points of straight chain hydrocarbons are always higher than the branched-chain isomers, the values of smoke points became higher with increasing the polyethylene content of the feedstock. The freezing points changed similarly with the polyethylene content. The freezing point requirement of JET fuel standard was not fulfilled even so if the feedstock contained of 91 % isomer hydrocarbon.

Table 1: Main properties of the examined feedstocks

Properties	PP100	PE100	10PE90PP	20PE80PP	30PE70PP	50PE50PP
PE content, %	0	100	10	20	30	50
PP content, %	100	0	90	80	70	50
Density, kg/m^3	784	779	785	786	779	779
Freezing point, °C	-44.0	-24.2	-43.4	-37.3	-35.2	-34.2
Smoke point, mm	30.1	39.4	30.6	31.0	32.0	32.9
Iodine number, $gI_2/100g$	135	105	132	129	126	120
n-paraffin content, %	4.6	30.7	6.6	12.2	13.0	18.6
n-olefin content, %	4.4	47.1	10.2	14.0	17.0	23.4
isomer content, %	91.0	22.3	83.2	73.8	70.0	58.0

2.2 Catalyst preparation

SAPO-11 was hydrothermally synthesized using orthophosphoric acid, aluminium acetate, silica sol (Ludox® TMA), and dipropylamine as template. The synthesis gel was prepared as follows: aluminium acetate was added to the mixture of orthophosphoric acid and water with vigorous stirring at room temperature for 2 h and finally mixed with dipropylamine. The synthesis gel was kept in ice water and hydrothermally treated at 145 °C for 92 h. The crystalline product of the synthesis was washed with deionized water to neutral pH, then dried and calcined at 540 °C. In the first step of catalyst formulation kaolin, aluminium hydroxide sol (Nyacol® Al20SD) and water were added to the zeolite and cylindrical catalyst particles were extruded. The cylindrical particles were dried at room temperature, and then in a laboratory electric oven at 550 °C for 2 h.

Metal loading was carried out by wet impregnation with $Pt(NH_3)_4(OH)_2*H_2O$ solution. After impregnation for 24 h, the material was dried at 120 °C and finally calcined at 480 °C for 4 h.

2.3 Catalyst characterization and properties

The concentration of Brønsted acid sites was determined by measuring the temperature-programmed ammonia evolution by heating the sample from 180 °C to 650 °C in nitrogen flow. The released ammonia was absorbed in water and titrated continuously with 0.1 M HCl solution. The ammonia released between 180 °C and 650 °C was taken as equivalent with the Brønsted acid site concentration of the sample. The specific surface area of the catalyst was determined from the nitrogen adsorption isotherm measured at -196 °C. Before the measurement the sample was out-gassed by evacuation at 200 °C for 3 h. The specific surface area was determined by the Brunauer-Emmett-Teller method.

Table 2: Main properties of the catalyst

Properties	Pt/SAPO-11
Platinum content, %	0.5
Brønsted acidity, mmol/g	0.45
Strength of Brønsted acid sites, °C	200 - 300
Specific surface area, m^2/g	320
Average pore diameter, nm	0.39 x 0.63

SAPO-11 catalyst had monodimensional pore system with nonintersecting elliptical 10-membered ring pores of diameter 0.39 x 0.63 nm (Table 2). The Brønsted acid sites concentration of the tested catalyst was 0.45 mmol/g. The ammonium form of the sample decomposed completely between 200 and 300 °C; therefore it contained weak Brønsted acid sites.

2.4 Catalytic experiments and analytical methods

Similarly to cracking hydrogenation and hydroisomerization were carried out in continuous operation mode. The apparatus contained all of the equipment and devices that can also be found in the reactor system of an industrial hydroisomerization plant (Hancsók et al., 2007). Before the catalytic run, catalyst was activated in-situ in the down-flow tubular reactor (effective volume: 100 cm^3) by reduction at 450 °C in hydrogen flow. The qualitative and quantitative analysis of feedstocks and liquid products were made by a GC equipped with a flame ionization detector and RTx-1 column. The densities, freezing- and smoke points of the feedstocks and the liquid products were measured according to standard analytical methods as EN 12185, ASTM D 5972 and ASTM D 1322.

3. Results and discussion

The products of the hydrogenation and hydroisomerization were the mixtures of liquid and gas phase hydrocarbons. The yield of liquid products obtained at 320 °C was 98 %. At higher temperatures hydrocracking reactions came to the front, therefore 8 % of C_1 - C_4 gaseous product was also formed at 360 °C. Production of gas phase hydrocarbons was also promoted by decreasing the LHSV, and increasing the residence time of molecules on the catalytically active sites. Methane and ethane were not identified in gas product even at the most stringent process parameters (T = 360 °C, LHSV = 1.0 h^{-1}). This suggests that, C – C bond hydrogenolysis did not occurred over metallic sites, but the hydrocracking and hydroisomerization reactions did proceed in the pores of the catalyst. The reaction mechanism of olefin hydrogenation and hydroisomerization is depicted in Figure 1. The reaction of an olefin with hydrogen may follow two reaction paths. In direct hydrogenation (k_1 and k_1') paraffin with the same skeletal structure as the starting olefin is produced. The alternate reaction path involves the formation of carbeniumion on the surface of the catalyst (k_2 and k_2'). This carbeniumion undergoes skeletal rearrangement (k_3) to give a mixture of secondary and tertiary carbeniumions. Skeletal rearrangement can be occurred with alkyl group or hydride ion shift (type A) or with formation of protonated cyclopropane intermediate (type B). In type A isomerization the branching degree of the carbeniumion is not modified, just their positions change. In type B isomerization the branching degree is increased or decreased (Bouchy et al., 2009). The rate limiting step is the rearrangement on the acidic sites. The adsorbed tertiary carbeniumion is favoured thermodynamically. Isoparaffins are formed form either linear or branched-chain olefins (Frye et al., 1963). The last reaction steps are desorption of olefins and their hydrogenation (Thybaut et al., 2005) at the metallic sites (k_4 and k_4'). In addition to the hydroisomerization hydrocracking may also occur at the acidic sites. Multi-branched isomers and the intermediates are particularly reactive; they are easily crack into smaller molecules reducing the product yield.

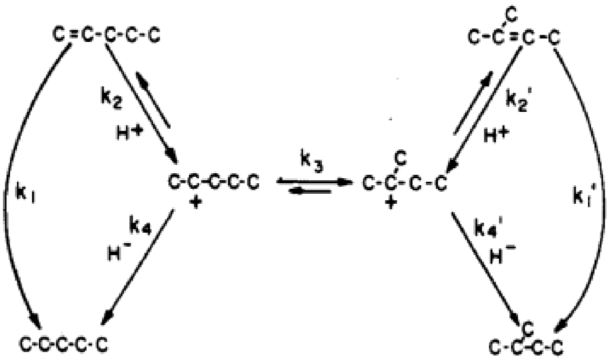

Figure 1: Reaction mechanism of hydrogenation and hydroisomerization of olefins

By increasing the temperature isoparaffin contents of the liquid products increased (Figure 2). At the examined process parameters olefin free kerosene fractions with 30.0 – 95.0 % isoparaffin contents were produced. In case of the 10PE90PP and PP100 feedstocks only minor hydroisomerization was occurred at 320 and 340 °C. At these temperatures the isoparaffin contents increased by 0.6 – 3.0 % (LHSV = 1.0 h^{-1}) and 0.0 – 2.0 % (LHSV = 2.0 h^{-1}). In case of the higher polyethylene containing feedstocks (20PE80PP, 30PE70PP, 50PE50PP, PE100) the isoparaffin contents increased significantly even at 320 °C ((5.8 – 10.2 % (LHSV = 1.0 h^{-1}) and 3.0 – 9.3 % (LHSV = 2.0 h^{-1})). The reason of this was that, hydroisomerization is an equilibrium reaction where the catalyst is capable of exerting isomerization activity until the reach of the equilibrium composition. The equilibrium composition is determined by the thermodynamics. The compositions of the 20 – 100 % polyethylene containing feedstocks were far from the equilibrium; therefore during their hydroisomerization thermodynamic inhibition could not be observed.

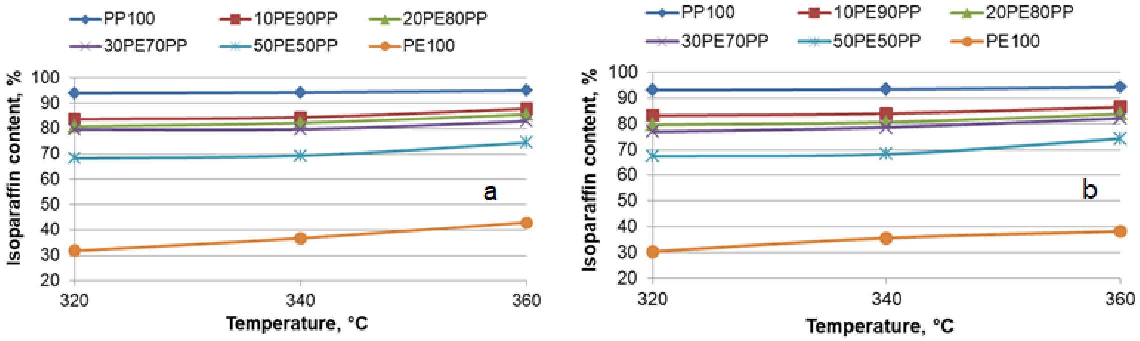

Figure 2: Isoparaffin contents of the liquid products (a: LHSV = 1.0 h^{-1}, b: LHSV = 2.0 h^{-1})

Due to the extraordinary conditions of aviation freezing point is one of the most important performance property of JET fuels. At low temperatures the precipitated paraffin crystals can cause severe operational disorders in JET engines. The maximum allowable value of the freezing point is - 47 °C. The freezing point values of the products of the hydrogenation and hydroisomerization (Figure 3) decreased with the increase of the isoparaffin contents. The lower molecular weight compounds formed in cracking reactions also improved the low temperature property. Accordingly, at the favourable process parameters (T = 360 °C, LHSV = 1.0 h^{-1}) the freezing point values were between – 57 °C and – 26 °C. The requirement of JET fuel standard was only fulfilled by products formed in the hydrogenation and hydroisomerization of PP100 feedstock. Burning properties of the feedstocks and the liquid products were characterized by smoke point. According to the JET fuel standard, the minimum value of the smoke point is 25 mm. The requirement of JET fuel standard was fulfilled by not only the feedstocks, but also the products (Figure 4). The examined feedstocks did not contain aromatic hydrocarbons. In addition in the hydroconversion reactions from the unsaturated hydrocarbons saturated ones were formed. Saturated hydrocarbons have higher hydrogen/carbon ratios and better burning properties. Liquid products with the highest smoke point values were produced from feedstocks contained isoparaffins in the smallest concentrations. The reason of this was that, the branched-chain hydrocarbons also decreased the smoke point values.

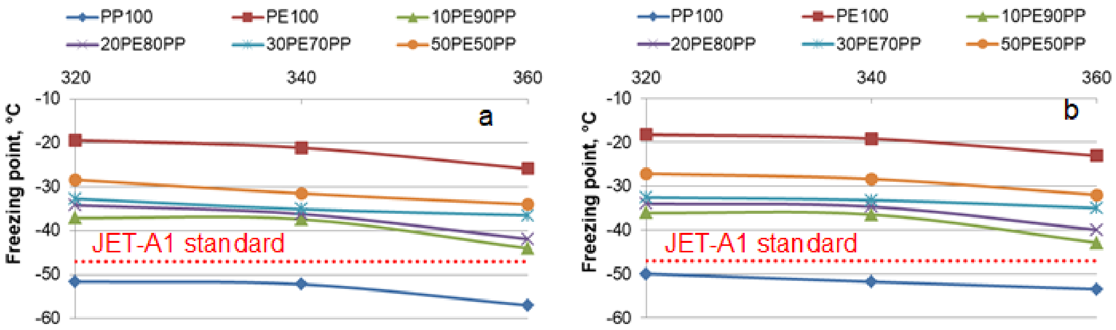

Figure 3: Freezing points of the liquid products (a: LHSV = 1.0 h^{-1}, b: LHSV = 2.0 h^{-1}, PP100: - 44.0 °C, PE100: - 24.2 °C, 10PE90PP: - 43.4 °C, 20PE80PP: - 37.3 °C, 30PE70PP: - 35.2 °C, 50PE50PP: - 34.2 °C)

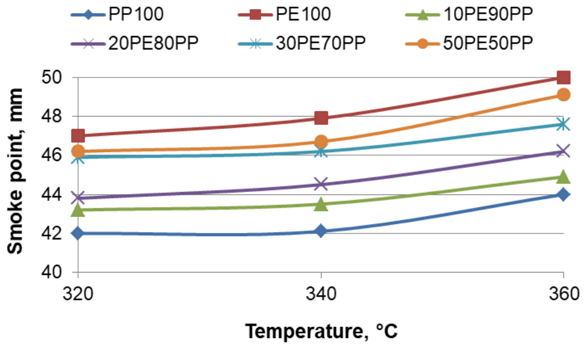

Figure 4: Smoke points of the liquid products (LHSV = 1.0 h^{-1}, PP100: 30.1 mm, PE100: 39.4 mm, 10PE90PP: 30.6 mm, 20PE80PP: 31.0 mm, 30PE70PP: 32.0 mm, 50PE50PP: 32.9 mm)

4. Conclusions

Hydrogenation and hydroisomerization of kerosene boiling point fractions of thermal cracking of polyethylene, polypropylene and those mixtures were examined on Pt/SAPO-11 catalyst. Experiments were carried out in continuous operation mode in the temperature range of 320 - 360 °C, 40 bar pressure, H_2 to hydrocarbon ratio of 400 Nm^3/m^3, and LHSV = 1.0 and 2.0 $h^{-1.}$ At the examined process parameters olefin free kerosene boiling point fractions with 30.0 – 95.0 % isoparaffin contents were produced. Due to the thermodynamic inhibition the extent of the hydroisomerization (0.0 – 3.0 %) was only minor in case of the PP100 and 10PE90PP feedstocks. The freezing point values of the products of the catalytic experiments decreased with the increase of the isoparaffin contents. At the favourable process parameters (T = 360 °C, LHSV = 1.0 h^{-1}) the freezing point values changed between - 57 °C and - 26 °C. The requirement of JET fuel standard was only fulfilled by products formed in the hydrogenation and hydroisomerization of PP100 feedstock. The smoke point requirement of JET fuel standard was fulfilled by not only the feedstocks, but also the products. Liquid products with the highest smoke point values were produced from 50PE50PP and PE100 feedstocks. Due to the inadequate freezing points and densities (766 kg/m^3 - 773 kg/m^3) the products of the experiments cannot be used directly as engine fuel, just only as high value blending components.

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