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CATALYTIC CRACKING OF POLYOLEFINES WASTE TO DIESEL OIL AND GASOLINE

Keywords

Catalytic cracking, plastic waste, diesel oil, gasoline.

Abstract

Polyethylene and polypropylene waste was cracked thermally or in presence of a catalyst. The obtained products were analysed by gas chromatography. The cracking of polyethylene gives linear carbon chain alkanes and alkenes. Presence of toluene was detected as well. This product is suitable as a component of diesel oil. The cracking of polypropylene produce branched carbon chain alkanes and alkenes. This product is suitable as a gasoline component.

Introduction

In Poland, plastic packaging market reached 488,000 tons in 2004 [1] and only 22.4% was recycled. Among plastic waste 65% are polyolefines and 15% polystyrene. Polymer recycling has been suggested as the only sustainable solution to the problem of the huge, rapidly increasing amount of plastic waste. Among the various polymer recycling methods, thermal and/or catalytic degradation of plastic waste to fuel shows the highest potential for future commercial polymer recycling process, especially as plastic waste can be considered as a cheap source of raw materials and depletion of natural resources progresses. Polyolefines and polystyrene can be cracked to liquid fuels like gasoline and diesel oil [2, 3]. Cracking can take place in the presence of the catalyst or without it. Catalytic cracking takes place approximately at 400°C, which is about 50°C lower than without the catalyst [4-8]. Thermal cracking gives a wider spectrum of products, including an unwanted product like coke, which hampers heat exchange in a reactor. The catalysts used have been mainly acid solids (zeolites, alumina, silica alumina). For cracking, bulky polymer molecules catalysts should have large pores or small grain size. In the latter case, the high proportion of external acid sites promotes polymer cracking while large pores favour reforming the primary products.

1. Experimental procedure

Plastic waste of polyethylene (PE), as a foil (LDPE), and as a granulate (HDPE), as well as polypropylene (PP), as a granulate and a foil. were used as raw materials. The cracking of polyolefines was carried out in a double reactor. The lower reactor was loaded with polymer and 10% of powdery catalyst prepared from Polish diatomite by activating it by etching in 18% hydrochloric acid and washing it in water. After drying at 100°C, diatomite was calcinated in an oven at 300°C. After activation, the specific surface area has increased from 52 to 151 m^2/g. Average grain size of the powder was 11 μm. The chemical composition was the following: SiO_2 90%, Al_2O_3 2.4%, the rest are carbonates of alkali metals and alkali earth metals.

The lower reactor, with capacity of 0.7 dm^3 was connected with the upper reactor with capacity of 0.2 dm^3 loaded with a catalyst in form of beads with a diameter of 3-5 mm. The catalyst acidic form of molecular sieves NK 10 was used. NK 10 contained A type zeolite with a pore size of 0.4 nm. The acidic form was prepared by ion exchange of sodium to ammonium cations and heat treatment at 400°C, so the removal of ammonium took place. In the lower reactor, the decomposition of polymer to hydrocarbon vapours took place. Hydrocarbon vapour flows to the upper reactor where further cracking occurred. The cracking product flows to a condenser where compounds with number of carbon atoms higher than 4 are condensed. Compounds with a lower number of carbon atoms leave condenser as a gas.

2. Results and discussion

The results of selected polyolefines cracking experiments and fractions of liquid products are presented in Table1. The boiling point of a gasoline fraction is lower than 170°C. Above this temperature and below 300°C diesel oil is collected. The residue is heating oil.

Table 1. Cracking conditions and fractions of liquid products

Polymer	Lower rector		Upper reactor		Efficiency /%/		
	Catalyst	Temperature /°c/	Catalyst	Temperature /°c/	Depolimerization	Gasoline Fraction	Oil Fraction
PP	+	350	+	450	100	60	30
PP	-	350	+	450	82,5	45	30
PP	-	390	-	450	90	wax	
PE	+	390	+	420	100	50	45
PE	+	500	-	450	100	55	40
PE	-	500	-	450	100	wax	

From data in the Table1, it is clear that without catalyst cracking product is waxy and temperature for cracking is higher than in catalyst presence. The temperature values for the experiments were chosen so that cracking rate was observable.

Grey powder in the first reactor (after cracking) is the catalyst covered by coke. The weight of coke does not exceed 5% of polymer weight. Applying two different catalysts for the degradation of polypropylene, the highest efficiency of conversion to the liquid product was obtained. Using only NK 10 catalyst in the upper reactor, the efficiency was lower, because not all of the polymer was depolymerised. The cracking of polyethylene over two different catalysts also gives the highest efficiency of liquid product. The composition of cracking product was established by chromatographic analysis, using Agilent Technologies 6890 N apparatus connected to the mass spectrometer 5973 N.

Composition of LDPE cracking product is listed in Table 2.

Tab. 2. Composition of LDPE cracking product

Compound name	wt. %	Number of carbon atoms	Type of hydrocarbon
1-hexene	20.4	6	Alkene
toluene	9.76	7	Aromatic
2,4-octadiene	0.9	8	Diene
1-nonene	3.96	9	Alkene
1-decene	3.98	10	Alkene
1-undecene	2.82	11	Alkene
undecane	0.98	11	Alkane
1-dodecene	2.91	12	Alkene
dodecane	1.22	12	Alkane
1-tridecene	2.67	13	Alkene
Tridecane	1.15	14	Alkane
1-pentadecene	2.85	15	Alkene
Tetradecane	1.1	14	Alkane
1-pentadecene	2.36	15	Alkene
Tetradecane	1.09	14	Alkane
1-heksadecene	2.12	16	Alkene
Heksadecane	1.12	16	Alkane
1-heptadecene	1.74	17	Alkene
Eicosan	1	20	Alkane
1-oktadecene	1.95	18	Alkene
Total	66.08		

Among the first twenty compounds, which constitute 66% of the total amount, 7.66% are alkanes, 9.76% aromatic compounds, and 48.66% alkenes.

Cracking of polypropylene in the same conditions produced a product, the composition of which is presented in Table 3.

Table 3. Composition of the PP cracking product

Compound name	wt. %	Number of carbon atoms
1,2-dimetylocyklopropane	2.81	5
4-metylo-2-pentene	6.55	6
3,4-dimetylo-(Z)-2-pentene	5.32	7
4-metyloheptane	11.79	8
1,2,3-trimetylocyklopentene	3.08	8
propylocyklohexane	8.8	9
2,4-dimetylo-1-heptene	4.02	9
2,4,6-trimetylo-3-heptene	3.02	10
2-metylo-3-etylo-2-heptene	1.1	10
2,6-dimetylo-3-octene	1.56	10
cis-4-decene	1.55	10
2,6-dimetylo-3-octene	1.07	10
2,6-dimetylo-[S-(E)]-4-oktene	2.31	10
2,6-dimetylononane	2.32	11
(E)–5-undecene	0.97	11
2,3,6-trimetylo-4-octene	1.46	11
2,3,6,7-tetrametylo-4-octene	1.21	12
2,4-dimetylo-2-decene	2.42	12
1,2-dietylo-3-metylocyklohexane	0.81	11
heptylocyklohexane	1.08	13
total	63.25	

Among the listed compounds are 14.1% alkanes, 32.56% alkenes and 16.58% cyclic hydrocarbons. There are differences in the composition of cracking PE and PP. The first difference is that alkanes and alkenes from PE have linear carbon chains while from PP they are branched. The presence of toluene results from the cyclization and aromatisation of the linear carbon chain. The second difference is that compounds from PE have a higher number of carbon atoms and alkanes have a unsaturated bond at the first carbon atom. For unsaturated hydrocarbons from PP, the double bond is located in from 1 to 4 carbon atoms. Product distribution for PE and PP cracking is presented in Fig.1.

There is a difference in the product distribution for polyethylene cracking and polypropylene cracking. For PE, the maximum concentration is for compounds with 6 carbon atoms and above 9 carbon atoms, the concentration of compounds is almost constant. For PP, there is a broad peak of the highest concentration compounds having 8, 9, 10 carbon atoms.

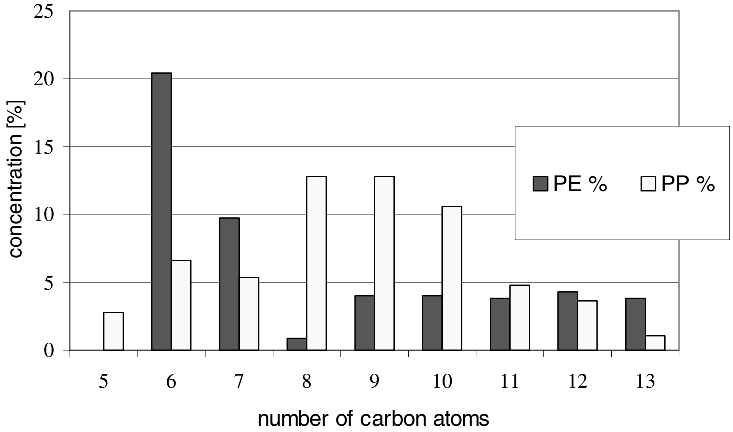

Fig. 1. Product distribution in the polyethylene and polypropylene degradation

Real plastic waste contains at least PP and PE, so in the next experiment, a mixture of 80% PE and 20% PP was used as a raw material. After cracking in the first reactor at 400°C and 400°C in the second reactor, the liquid product was obtained with efficiency of 71%.

The cracking product was distilled into a gasoline fraction (boiling temperature < 170°C) and an oil fraction (boiling temperature above 170°C and lower than 300°C).

The selected properties of the gasoline fraction obtained from polyethylene and polypropylene (1:1) are as follows:

– density d_{20}, g/cm^3	0.68
– initial boiling point, °C	35
– volume distilled to 70°C, %	35
– volume distilled to 150°C, %	90

Selected properties of oil fraction are as follows:

– density d_{20}, g/cm^3	0.795
– viscosity, 25°C, mm^2/s	3.32
– volume distilled to 250°C, %	65
– volume distilled to 300°C, %	90

Gasoline and oil have a lower density than required by Polish Standards [9, 10], but this is not a problem if these fuels are mixed with commercial fuels. Gasoline and oil were tested on a Honda 450 gasoline fuelled generator and on diesel engine in Institute for Sustainable Technologies, Radom. There was no difference in load speed characteristic for commercial fuels with addition of 50% gasoline or oil from cracking plastic waste. Studies of octane number and cetane number are in progress. Results of toxicity of exhaust gases for gasoline with various additions of gasoline from plastic waste (for different engine loads) is presented on Fig. 2.

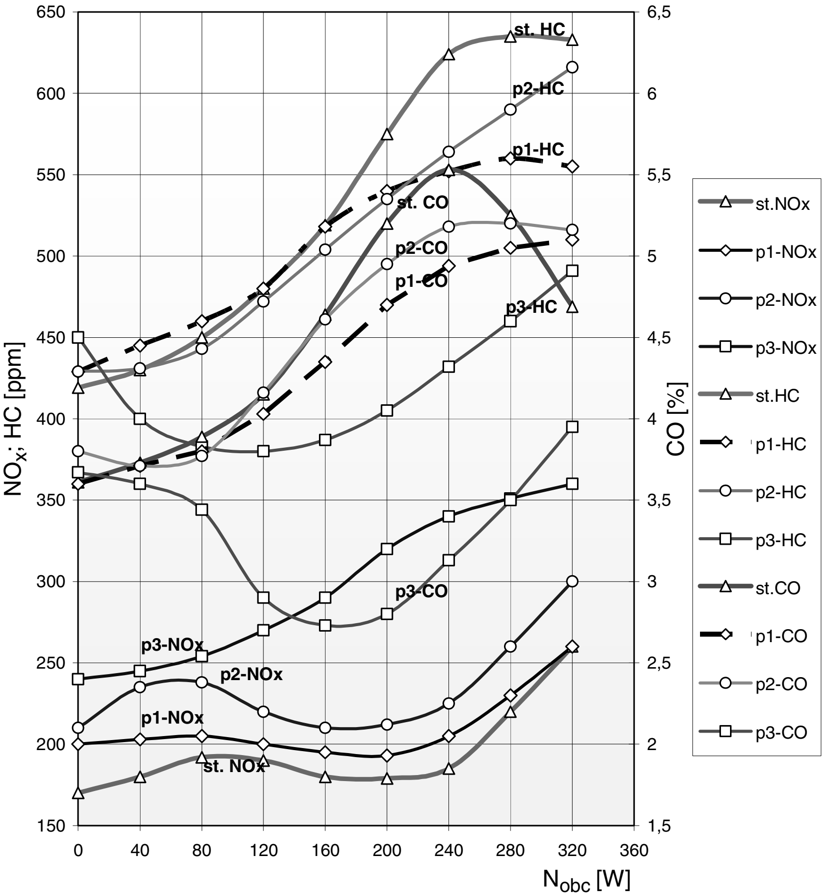

Fig. 2. The dependence of concentration of toxic components of exhaust gases on engine load: st. – standard gasoline, p1 – standard gasoline plus 20% gasoline from plastic waste, p2 – standard gasoline plus 50% gasoline from plastic waste, p3 – 100% gasoline from plastic waste

Relations on Fig. 2 show that there are decreases of carbon monoxide and hydrocarbon emission for gasoline with the addition of gasoline from plastic waste. For nitrogen oxide, there is increase of emission, but with an addition of 20% this increase is small.

Conclusions

- Cracking polyolefines in the presence of catalysts (diatomite and molecular sieve NK 10) produces a liquid product with a high efficiency.
- The product of PE cracking contains alkanes and alkenes with linear carbon chains, which are desirable as a diesel oil component because of their high cetane number.

- The product of PP cracking contains alkanes and alkenes with branched carbon chains, which are desirable as a gasoline component because of high octane number.
- The emission of carbon monoxide and hydrocarbons is lower for gasoline with the addition of gasoline from plastic waste. Nitrogen oxide emission is a little higher.

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Reviewer:
Zenon M. SARBAK

Katalityczny kraking odpadów poliolefinowych do oleju napędowego i benzyny

Słowa kluczowe

Kraking katalityczny, odpadowe tworzywa sztuczne, olej napędowy, benzyna.

Streszczenie

Odpady polietylenu i polipropylenu krakowano z udziałem i bez udziału katalizatora. Uzyskane produkty analizowano chromatograficznie. Kraking polietylenu daje alkeny i alkany o prostym łańcuchu węglowym. Obecny w produktach krakingu był toluen. Produkty te są korzystne jako komponenty oleju napędowego. Produktami krakingu polipropylenu są alkeny i alkany o rozgałęzionym łańcuchu węglowym, co jest korzystne jako komponent benzyny.