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HYDROCRACKING USED TO PROCESS POLYOLEFIN WASTES

HYDROKRAKING W PRZETWÓRSTWIE ODPADOWYCH POLIOLEFIN

Abstract

The paper presents results of tests connected with hydrocracking processes of fluid products of polyolefin wastes pyrolysis. The material contained 30–55% v/v of components with boiling range below 360°C. Two catalysts, NiW, were used. The catalyst worktime, temperature and pressure were tested in aspect of their influence on fraction composition of the products.

Keywords: polyolefin wastes, fuel fractions, hydrocracking

Streszczenie

W artykule przedstawiono wyniki badań związanych z procesem hydrokrawingu ciekłych produktów pirolizy odpadowych poliolefin. Materiał zawierał 30–55% v/v składników o temperaturze wrzenia poniżej 360°C. W badaniach wykorzystano dwa katalizatory NiW. Badano wpływ ciśnienia oraz czasu pracy katalizatora na skład frakcyjny produktu.

Słowa kluczowe: odpadowe poliolefiny, frakcje paliw, hydrokrawing

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1. Introduction

As generally prognosed nowadays, there may be shortages of fluid fuels, especially diesel oil, in the near future. Polyolefin wastes may successfully be used as an alternative source of fuel fractions. Necessary processing to obtain fuels consists of two stages. Stage one (pyrolysis), conducted at 350–400°C, is to transform approximately 90% m/m of the material into fluid products with capacity 80–85% m/m on average. The products undergo complete distillation when below 360°C, do not contain heteroatoms (chiefly sulphur), and the percentage of unsaturated components is 40–50% m/m. In order to obtain high-value fuel fractions, it is necessary to add stage two (hydrogen purification) on hydrorefinement or hydrogenation catalysts.

Another variant form of polyolefin waste processing is pyrolysis together with kerosene related oils. This form was used on a commercial scale by Agrob-Eko in Zabrze and Rafineria Jasło S.A. In final effect, they obtained fluid products or partially crystallizable products containing approximately 20% m/m of unsaturated components. An unfavourable feature of the products was that they contained sulphur (0.3–0.5% m/m) and that the level of components with petrol and diesel oil boiling ranges was merely 30–55% v/v. Therefore it seemed reasonable to undertake research on hydrocracking processes for the purpose of increasing capacity of fractions with petrol boiling range (up to 200°C) and diesel oil boiling range (200–360°C).

2. Experimental section

2.1. Test materials

Test materials used for hydrocracking processes were two fluid products obtained on Agrob-Eko installation. The products were very different in respect of fraction composition. One of them (**S I**) contained approximately 45% v/v of components undergoing distillation above 360°C, whereas the other (**S II**) contained 70% v/v of such components. Hence **S II** had higher density, higher average molecular mass and higher sulphur content compared with **S I**. On the other hand, both products had similar percentage of sulfonable compounds (below 20% m/m). Physical and chemical properties of the materials are shown in Table 1. Fraction composition is presented graphically in Fig. 1.

Table 1

Physical and chemical properties of materials S I and S II

PARAMETER	S I	S II
Density d_4^{20} g/cm ³	0.825	0.848
n_D^{20}	1.461	1.470
M_{av} g/mol	228	281
Percentage of sulfonable Compounds % m/m	17	14
Sulphur content % m/m	0.25	0.41

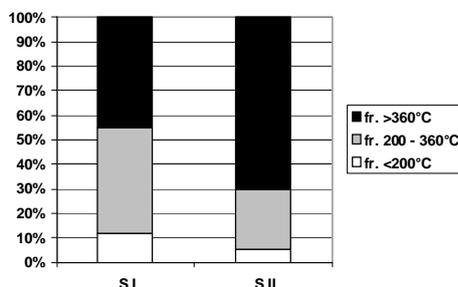


Fig. 1. Fraction composition of materials **S I** and **S II**

Rys. 1. Skład frakcyjny surowców **S I** i **S II**

2.2. Testing methods

Hydrocracking processes were conducted in a flow pressure unit on solid catalyst bed. Two nickel-wolfram (NiW) catalysts were used. One of them (K1) was a test catalyst, prepared by Wrocław Technical University for polycyclic conversion of aromatic hydrocarbons. The other (HC-26) was a commercial catalyst, produced by Refinery of Płock. Parameters of the processes were as follows:

- temperature – 350 and 450°C,
- pressure – 6 and 8 MPa,
- catalyst mass load – 2 to 2.4 h⁻¹.

Hydrocracking for material **S I** was conducted on catalyst K1, and for material **S II** (except one process) was conducted on catalyst HC-26. Eight processes were conducted on each catalyst. Total amount of the material under hydrocracking at the same time was 250 ml. One process lasted approximately 2 hours, so each catalyst worked overall for several dozen hours. The tests enabled to define the changes in fraction composition of each material according to catalyst worktime, temperature and pressure used for the processes.

2.3. Results

2.3.1. Material **S I**

Results of tests performed on hydrocracking processes for material **S I** on catalyst K I are presented graphically in Fig. 2. The whole series was performed under 6 MPa.

The first three tests were performed at 350°C. The process on fresh catalyst was very effective. Capacity of the product obtained was 85% v/v. As shown in column no. **1**, components undergoing distillation below 200°C have the biggest share. The share increased nearly six times compared with the material. During the process there were some problems with correct dosing as the material tended to crystallize. To prevent quick crystallization, an amount of 20% v/v of toluene was added. Thus fraction composition of the material changed considerably (column **S I (T)**). The other two processes (columns **2** and **3**) gave higher capacity of products (90–95% v/v), but catalyst effectiveness gradually decreased. Therefore it was decided that the temperature should be raised up to 450°C. The

result was evident immediately (column 4). Fig. 2 indicates that activity of the catalyst became fairly stable upon about 12 hours of work. The share of petrol fraction in products (columns 6–8) was approximately 40% v/v i.e. several dozen per cent higher than in material **SI** (T). The share of components undergoing distillation above 360°C decreased by the same.

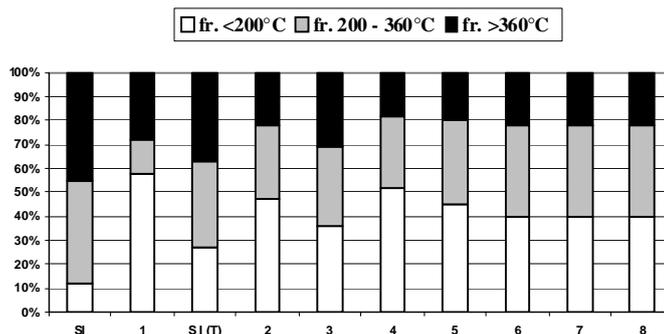


Fig. 2. Results of hydrocracking processes conducted for material **SI** on catalyst K I (1–8 process numbers, **SI(T)** material diluted with toluene)

Rys. 2. Wyniki procesów hydrokrakingu surowca **SI** na katalizatorze K I (1–8 numery procesów, **SI(T)** surowiec rozcieńczony toluenem)

2.3.2. Material **SI**

Further testing referred to hydrocracking processes on material **SI** and catalyst HC-26. The first four tests were performed at 350°C, and the other at 450°C. Most of the tests were performed under 6 MPa (the last one under 8 MPa). Before placing in the unit, the material was heated to prevent its crystallization, problems with dosing and necessity to add a solvent. Results of the tests are shown in Fig. 3.

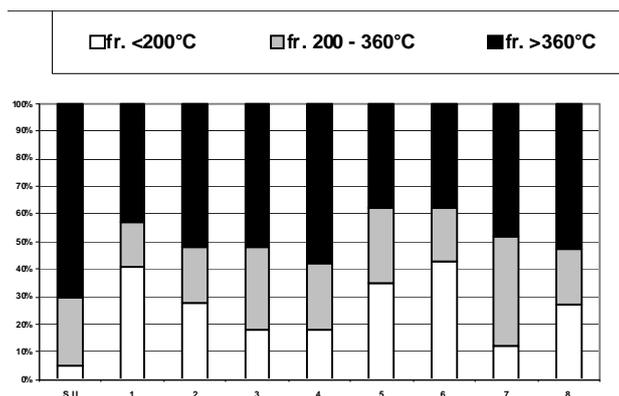


Fig. 3. Results of hydrocracking processes conducted for material **SI** on catalyst HC-26 (1–8 process numbers)

Rys. 3. Wyniki procesów hydrokrakingu surowca **SI** na katalizatorze HC-26 (1–8 numery procesów)

On completing the first process, conducted on fresh catalyst, a product with capacity approximately 70% v/v was obtained. Capacities of the other processes were higher (75–80% v/v). As in case of the previous material, this time the first process was very effective (column 1 in Fig. 3.). The share of fractions with petrol boiling range increased nearly eight times compared with the material, whereas the share of fractions with diesel oil boiling range decreased by approximately 8% v/v and fraction boiling above 360°C by approximately 27% v/v. The other three tests (columns 2–4) revealed that effectiveness of the processes gradually decreased. This situation was improved upon introducing higher temperature. Result of process 6 (column 6 in Fig. 2.) is evidently the same as that of process 1, apparently because the pump stopped pumping the material during the process thus breaking the process for about an hour. That is why the material remained longer in the reactor. The last process, conducted under 6 MPa (column 7) resulted in the following product:

- 12% v/v of fraction with boiling range below 200°C (over twice more than in the material),
- 40% v/v of fraction with boiling range 200–360°C (by 15% v/v more than in the material),
- 48% v/v of fraction with boiling range above 360°C (by 22% v/v less than in the material).

The lightest fraction can be obtained upon increasing the pressure (column 8).

A comparison was made during the tests between the two catalysts in aspect of their effectiveness for material **S II** when the processes were conducted at 450°C and under various pressures. The catalysts were used for several dozen hours. The results are shown in Figs 4 and 5.

Basing on the figures, it appears that catalyst HC-26 was more effective for the processes under 6 MPa, giving higher conversion of heaviest components of the initial material and higher share of fraction with diesel oil boiling range. Differences in effectiveness between the catalysts become smaller upon increasing the pressure. However, catalyst HC-26 tends to make the hydrocracking process create the components undergoing distillation up to 200°C. This is confirmed by physical and chemical properties of the products. Table 2 shows some basic physical and chemical properties of material **S II** hydrocracking products (catalysts K I and HC-26, pressure 8 MPa).

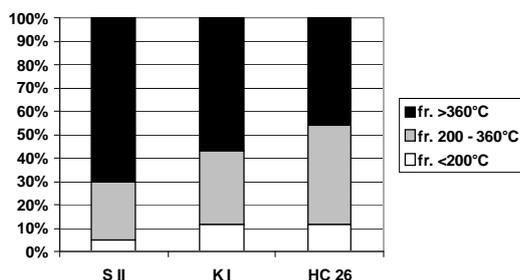


Fig. 4. Comparison between the catalysts in aspect of their effectiveness (pressure 6 MPa)

Rys. 4. Porównanie efektywności użytych katalizatorów (ciśnienie 6 MPa)

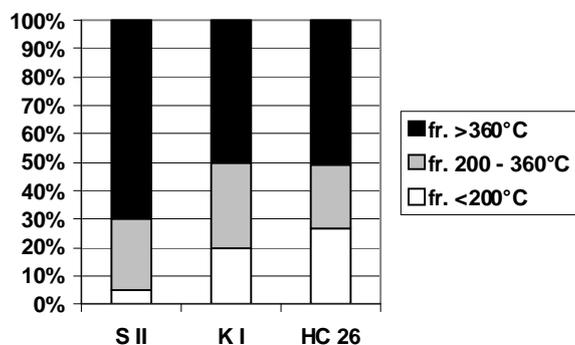


Fig. 5. Comparison between the catalysts in aspect of their effectiveness (pressure 8 MPa)

Rys. 5. Porównanie efektywności użytych katalizatorów (ciśnienie 8 MPa)

Table 2

Physical and chemical properties of material S II hydrocracking products

Parameter	Product obtained on catalyst K I (450°C, 8 MPa)	Product obtained on catalyst HC-26 (450°C, 8 MPa)
Density d_4^{20} g/cm ³	0.83	0.825
n_D^{20}	1.461	1.457
M_{av} g/mol	228	182
Percentage of sulfonable Compounds % m/m	15	20
Sulphur content % m/m	0.1	0.1

3. Summary

We performed a series of tests to find out if it was possible to obtain more fuel fractions through hydrocracking processes on industrial products and pyrolysis of polyolefin wastes. The results are considered moderately positive. Apart from tests performed on fresh catalysts, we managed to reduce the share of heaviest components, undergoing distillation above 360°C by 15% v/v for material S I and by up to 22% v/v for heavier material S II. Catalyst HC-26 was found to be more active. When used under lower pressure, it made the process create fractions with diesel oil boiling range. Higher pressures lead to deeper conversion of the material into petrol fraction.

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