ELSEVIER

Catalysis Today 65 (2001) 323–330

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Thermal and catalytic conversion of waste polyolefines

Jerzy Walendziewski*, Mieczysław Steininger

Institute of Chemistry and Technology of Petroleum and Coal, Wrocław University of Technology, ul. Gdańska 7/9, 50-344 Wrocław, Poland

Abstract

Waste samples of polyethylene and polystyrene were cracked thermally or in the presence of catalyst and hydrogen in closed autoclaves. The obtained products were submitted to analysis, unsaturated hydrocarbons in gasoline and diesel fuel range boiling were hydrogenated over platinum catalyst. It was stated that the optimum thermal cracking temperature of waste polyolefines is 410–430°C, in the case of catalytic process lower temperature, ca. 390°C, can be used, with reaction time ca. 1.5 an hour. More than 90% yield of gas and liquid fractions with b.p. $<$ 360°C was attained. The dependencies between process parameters, feed composition and product yield as well as composition of the obtained fuel fractions were found. On the basis of the obtained results hypothetical continuous process of waste plastics processing for engine fuel production was presented. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Waste plastics; Cracking; Hydrocracking; Catalyst; Fuels

1. Introduction

Thermal or catalytic cracking of waste plastics is one of the possible methods of their utilization [1–8]. As a result of the cracking at 400°C or higher process temperature some quantities of hydrocarbon mixtures in the form of gas, liquid products (gasoline and diesel fuel boiling range) as well as higher boiling liquid residue or solid can be obtained [1,6,8]. All these products can be used as fuels or fuel components. Especially liquid products of gasoline and diesel fuel boiling range can be applied as components of engine fuels. It is however necessary to remember that products of cracking or pyrolysis of polyolefines are highly unsaturated and therefore they have to be further submitted to hydrogenation and skeletal isomerization if they are to be applied as engine fuels. Application of cracking or hydrocracking catalyst and higher process temperature can enlarge conversion of waste plastics. The main goal of application of hydrocracking catalyst and hydrogen is hydrocracking of plastics and hydrogenation of olefins in process products. Taking into account these premises in these studies waste samples of polyethylene and polystyrene were used as raw materials in thermal or catalytic cracking and hydrocracking of polyolefines in the presence of catalysts. Process products were submitted to analysis, unsaturated hydrocarbons in gasoline and diesel fuel range boiling were hydrogenated over platinum catalysts.

2. Experimental

2.1. Materials

Waste samples of polyethylene and polystyrene were used as raw material. Cracking of polyolefines was carried out in autoclaves (volume: 1 dm^3) placed in a rotary kiln (10 min^{-1}). Autoclaves were equipped with pressure and temperature measurement systems

---

* Corresponding author.
Tel./fax: +48-71-322-1580, +48-71-320-3551.
E-mail address: walendziewski@nafta1.nw.pwr.wroc.pl
(J. Walendziewski).

PII: S0920-5861(00)00568-X

as well as the systems of pressurise and depressurise. Two kind of catalysts were applied in these studies: hydrocracking catalyst, containing NiW and 10% of HY zeolite, and waste commercial fluid cracking catalyst.

2.2. *Cracking and hydrocracking of waste plastics*

The plastic scrap feeds (25–100 g) were placed in the autoclaves and then if necessary solvent such as propane–butane, heptane or diesel fuel was added. A part of the experiment was carried out without any solvent but with addition of cracking or hydrocracking catalysts (0.3–0.5 wt.% in relation to the weight of plastic). The autoclaves with plastic feeds were fed with hydrogen up to the pressure ranging from 2 to 5 MPa. The autoclaves were rotated and heated up to the reaction temperature, 370–450°C, ca. 3 h and next their temperature was held constant for 0.5–2 h. After finishing of the reaction cycle the autoclaves content was cooled to ambient temperature, the valves were opened and gaseous products of reaction were directed to gas containers, submitted for measuring volume, density and chemical composition using gas chromatography. Liquid and solid parts of autoclaves content was weighed and submitted for determination of normal distillation, gas chromatography and bromine number. Molecular mass of solid and liquid products residue was determined. During plastics processing, after finishing the tests, autoclaves were cooled down to temperature 360°C and depressurised. Vapours of reaction products of this temperature were flowing through water cooler, gas products were collected in gas reservoir and liquids in receiver.

In the next step liquid products of polyolefines cracking, gasoline fraction with boiling point $<180°C$, was submitted for hydrogenation using noble metal based catalysts in flow micro-reactor apparatus ($3\,cm^3$ of catalyst, 3 MPa, 280–320°C). The hydrogenation and hydrocracking studies were carried out in continuous flow apparatus (OL: 115) equipped with feeding, temperature controlling, as well as gas and liquid products receiving systems.

2.3. *Determination of physicochemical properties of the obtained products*

- Chemical composition of gas products was determined by chromatography method, gas chromatograph N503, FID detector, Porapak Q + S, 2.5 column.
- Chemical and fraction composition of liquid gas products was determined by chromatography method, gas chromatograph CHROM 4, FID detector, capillary column, 30 m, phase OV-17.
- Normal distillation of liquid products of cracking of polyolefines was made according to Polish Standard PN-67/C-04010.
- Aromatics content in liquid products was determined by IR method, Carl Zeiss Jena apparatus, Model M80, measuring absorption band 1600–1610 cm^{-1} and calculating according to the formulae:

$$C_A\,(\%) = 0.22 + 10.4 * K_{1610}.$$

- Bromine number, as an indicator of olefins content was determined according to ASTM-D 1491-60 (1971).

3. Results

3.1. *Influence of process parameters on reaction product distribution*

The results of selected polyolefines cracking experiments are presented in Figs. 1–5. It was found that thermal or catalytic processing of polyethylene in the temperature range 370–450°C resulted in appreciable level of its depolymerization depending on temperature, applied catalyst and reaction time. As a result of polyethylene cracking it was possible to obtain 1–30% solid residue, 10–70% liquid products of bromine number up to 100 g Br_2/100 g and gas. The weight of individual products depends on reaction time and temperature. It was found that average molecular weight of the obtained residue is in the range 300–500. However this product is unstable and can be further easily cracked, even in the course of distillation. Application of the lowest process temperature and/or short reaction time gave only small volume of gases and liquids, the main products of reaction was solid with limited solubility in heptane. Fig. 1 presents results of thermal cracking of polyethylene. In the lowest process temperature, relatively high volume of gas and weight of residue were produced, ca. 20%. Increase in process temperature results in not too large increase in gas

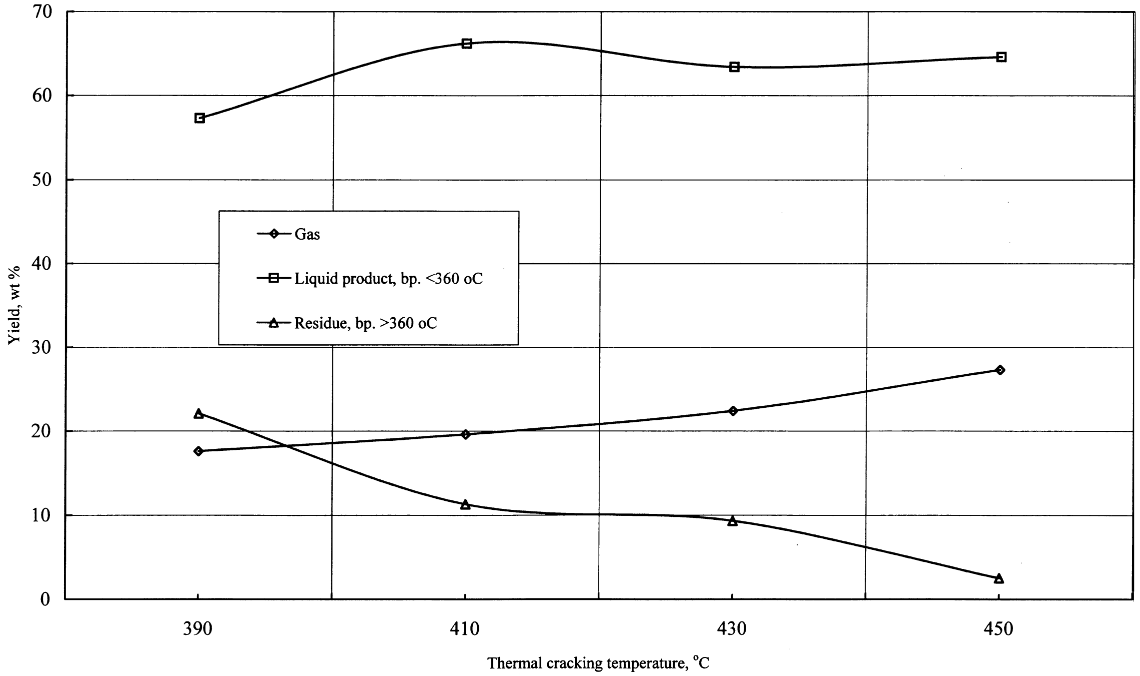

Fig. 1. Influence of reaction temperature on product composition of thermal cracking process of waste polyetheylene.

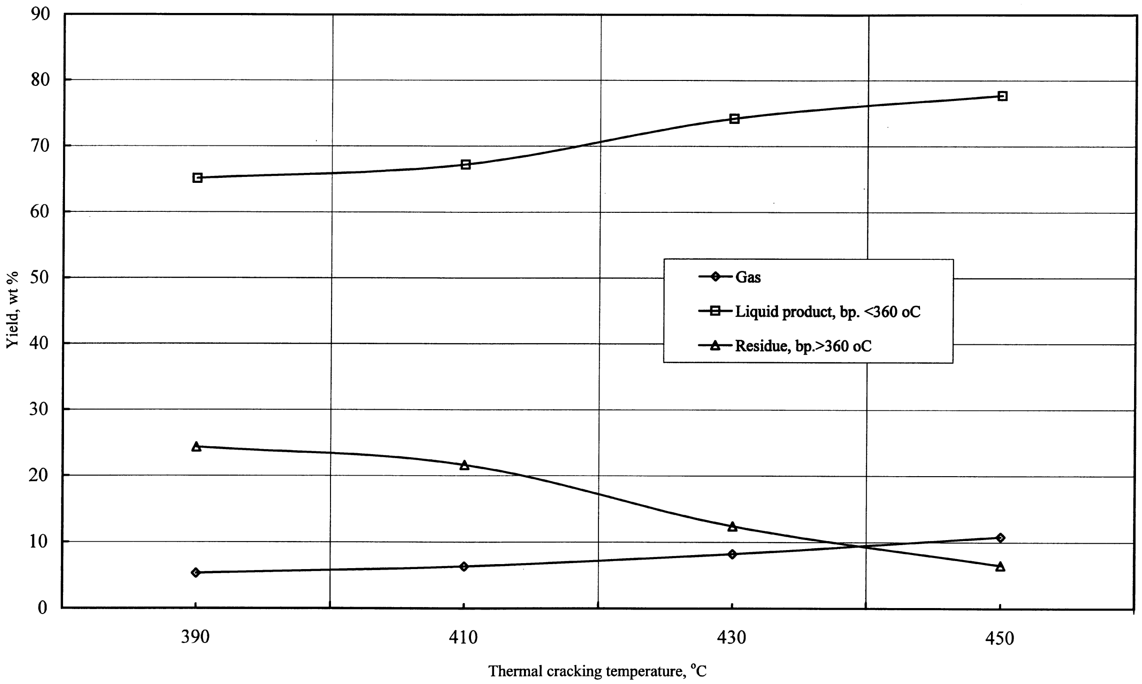

Fig. 2. Influence of reaction temperature on product composition of thermal cracking process of waste polystyrene.

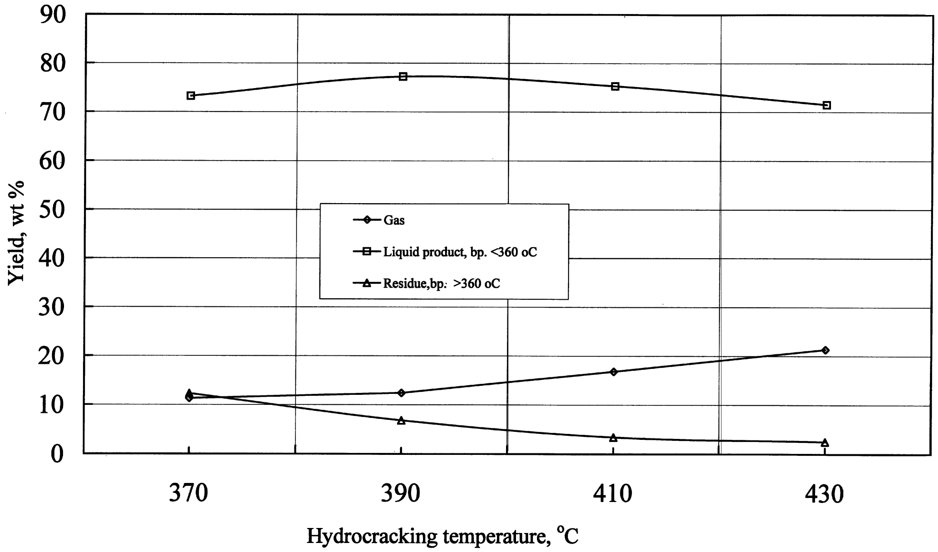

Fig. 3. Influence of temperature on product composition of hydrocracking process of waste polyethylene.

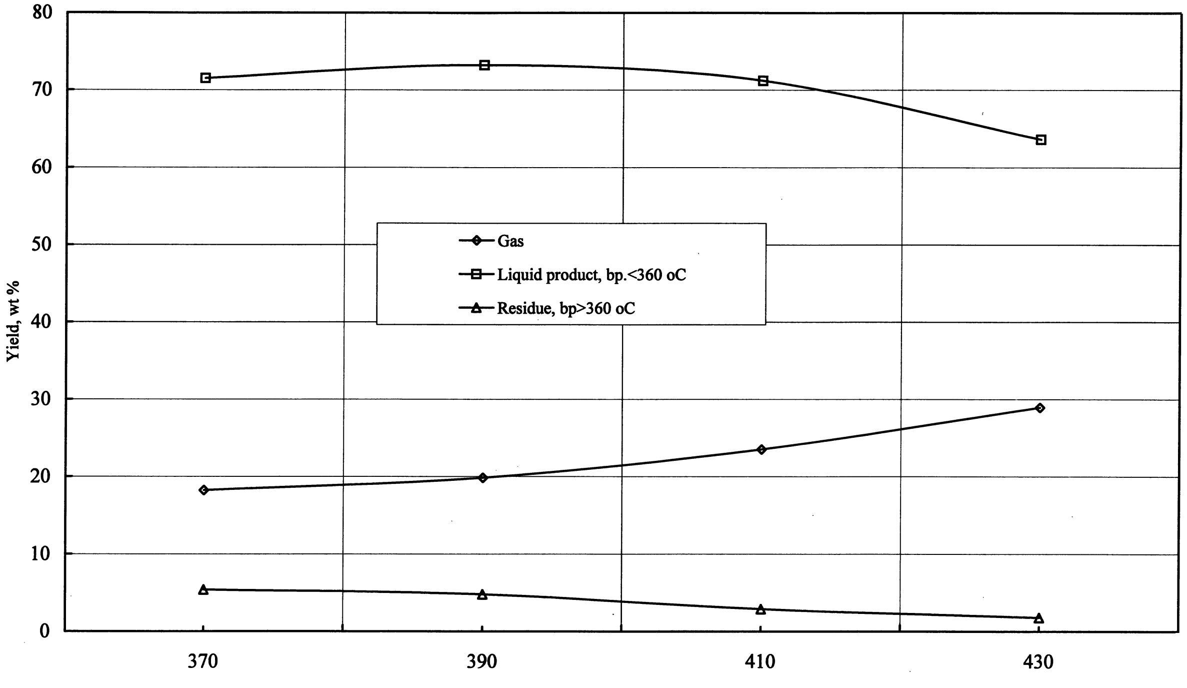

Fig. 4. Influence of temperature on product composition of catalytic cracking process of waste polyethylene.

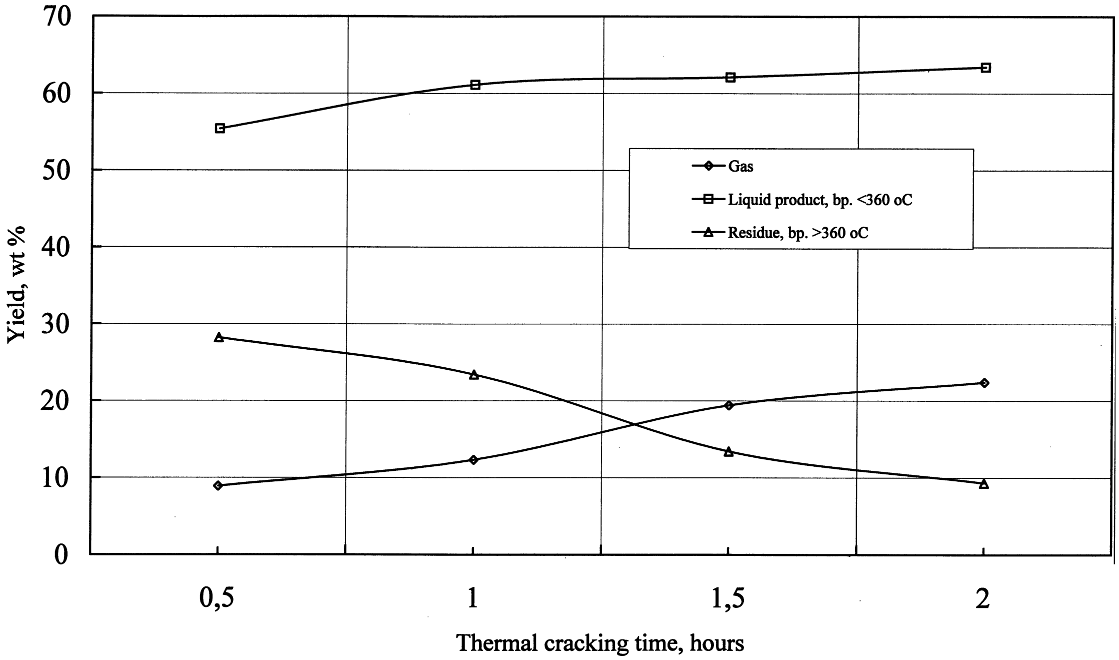

Fig. 5. Influence of reaction time on product composition of catalytic cracking process of waste polyethylene (temperature: 430°C).

volume and strong decrease in residue weight (2–3 wt.% at 450°C). Thermal cracking of polystyrene gives, as a rule, smaller volume of gas, from 2 to 10% and relatively large shares of residue (Fig. 2). It was found that at highest process temperatures besides the gas and liquid products, only solid, coke-like residue was obtained. Application of hydrocracking and cracking catalysts enables to lower the process temperature. One can see that application of cracking catalyst makes it possible to lower the process temperature by 20°C (Figs. 1 and 3). Similar results, lowering of process temperature, were obtained in the case of application of hydrocracking catalyst (Fig. 4). It is necessary to underline low share of residue and highest share of gas in reaction products in comparison with earlier discussed results (Figs. 1–3). Further results revealed, rather, small influence of catalyst content (in the range 0.3–1 wt.%) on process efficiency.

The influence of reaction time on product distribution is presented in Fig. 5. In order to minimise residue weight in reaction products it is necessary to apply at 1–1.5 h reaction time. However, these results can be mistaken because of relatively long time (ca. 3 h) necessary for heating of autoclaves to the reaction temperature.

3.2. Liquid products composition and properties

Liquid products of waste polyethylene cracking are complicated mixture of hydrocarbons (Table 1). They contained both paraffins and olefins as well as some quantity of aromatic hydrocarbons. The higher the temperature and the higher the reaction time — the higher aromatics content in liquid products. It was found that the main product of polystyrene cracking was BTX hydrocarbons, ethylbenzene and styrene.

However, the most surprising fact is that according to the spectral (IR) determination, 13–27% of aromatics (mainly BTX and styrene) was determined in liquid products from polyethylene cracking. This is in agreement with GC analysis (Table 1) and it means that almost all aromatics are contained in gasoline fractions.

In comparison with thermal and catalytic cracking process application of hydrocracking catalyst and hydrogen pressure resulted not only in higher gas and lower liquid product yield but also in lower olefin

Table 1
Composition of liquid products from cracking of polyolefines (reaction temperature 410°C)

Fraction/component	PE (TC) (wt.%)	PS (TC) (wt.%)	PE + PS (TC) (wt.%)	PE (CC) (wt.%)	PE (HC) (wt.%)
<180	72.4	100	92.3	78.1	84.0
180–220	16.4	–	4.8	4.8	3
>220	11.2	–	2.9	17.1	13
Benzene	1.1	4.0	3.6	1.5	0.7
Toluene	10.6	24.8	25.1	12.3	3.5
C_8 aromatics	18.1	65	41.8	15.2	4.8

content, bromine number from 1 to 3 g Br_2/100 g. Both in the case of thermal and catalytic cracking the obtained products contained large weight of olefins, lower in the case of cracking of polystyrene bromine number from 3.5 to 5 g Br_2/100 g , than polyethylene from 9 to over 100 g Br_2/100 depending on process parameters. In the case of mixed feed (50% PE+50% PS) bromine number attained values between 10 and 20 g Br_2/100 g.

3.3. Gas products composition

Gas products of both catalytic and thermal cracking as well as hydrocracking mainly consisted of methane, ethane and propane, smaller volume of C_4–C_6 hydrocarbons were also found. In the case of cracking, in the absence of hydrogen some content of olefins, mainly ethylene was stated. In comparison with cracking of polyethylene the main gas product of polystyrene cracking was methane, more than 40%, volume of other gas components was distinctly lower (Table 2). Because of high aromatic content in reaction products C_6–C_7^+, content in gas from polystyrene cracking products was also relatively high. As a rule C_1–C_3 hydrocarbons content in gas fraction attained a value 70–80%.

3.4. Hydrogenation of gasoline fraction

Gasoline and diesel fuel fractions are highly unsaturated and further hydrogenation step is necessary. It was showed that application of typical hydrogenation Pt/Al_2O_3 catalyst for hydrogenation of olefins in gasoline fraction (b.p. $< 180°C$) makes it possible to lower bromine number from 60–70 to less than 0.5 g Br_2/100 g (Table 3).

3.5. The continuous waste processing

In order to obtain engine fuels from waste plastics in one step it is necessary to apply continuous process. The proposal of continuous method of waste plastics processing is presented in Fig. 6 [9]. Waste plastics after washing, segregation and cutting are dosed to the EXTRUDER. The screw EXTRUDER supplies the mixed plastic scrap to the cracking reactor

Table 2
Composition of hydrocarbons in gas products from cracking of polyolefines (reaction temperature 400°C)[a]

Component	PE (TC)	PS (TC)	PE + PS (TC)	PE (CC)	PE (HC)
Methane	22.7	40.1	27.3	12.4	21.1
Ethane	27.4	23.3	23.1	20.4	21.2
Ethylene	1.4	2.0	1.0	2.3	0.1
Propane	26.6	15.0	20.1	30.4	23.7
Butane	11.0	8.6	14.0	20.3	20.7
C_5	6.9	1.9	6.1	5.6	7.3
C_6	2.1	5.8	4.8	3.3	3.8
$>C_7$	1.9	3.3	3.6	5.1	2.1

[a] PS, PE: polystyrene, polyethylene; TC, CC, HC: thermal and catalytic cracking, hydrocracking.

Table 3
Influence of process parameters on hydrogenation level of liquid fraction

T9 (°C)/p (MPa)/LHSV (h^{-1})	Gasoline fraction from thermal cracking of polyolefines, bromine number g Br_2/100 g		
	Polyethylene	Polystyrene	Polystyrene and polyethylene
Feed	29.2	2.8	13.0
280/3/2	0.5	0.3	0.3
320/3/1	0.1	0.03	0.05

CRACKER. At the reactor temperature 400–450°C the melted plastics are cracked and light hydrocarbons, gaseous and liquid products, are produced. The residence time of melted plastics in the reactor depends on the plastic type and the desired cracking extent.

The mixture of gaseous and liquid cracking products flows next to an EVAPORATOR in order to separate lighter hydrocarbon products from the high boiling residue. In order to easy evaporation and hydrogenation hydrogen-rich gas is also delivered to the EVAPORATOR. Evaporation level is a function of cracking product temperature, hydrogen flow velocity and total reactor pressure. It is desirable to apply such process parameters that allow evaporating fraction boiling up to 360°C. The hydrogen stream is composed of two streams, hydrogen from production plant and circulation gas, from the high-pressure SEPARATOR. High boiling residue, b.p. above 360°C, is continuously or periodically taken out from EVAPORATOR as fuel oil. The mixture of hydrocarbons and hydrogen from the EVAPORATOR is submitted to the CATREACTOR that contains hydrogenation catalysts (NiW, NiMo or Pd). Hydrogenation of olefins in fuel fraction takes place in this reactor in the temperature range 280–360°C. The CATREACTOR effluent is submitted for cooling and condensation in COOLER followed by the high-pressure SEPARATOR (and low-pressure SEPARATOR) and next to the product RECEIVER.

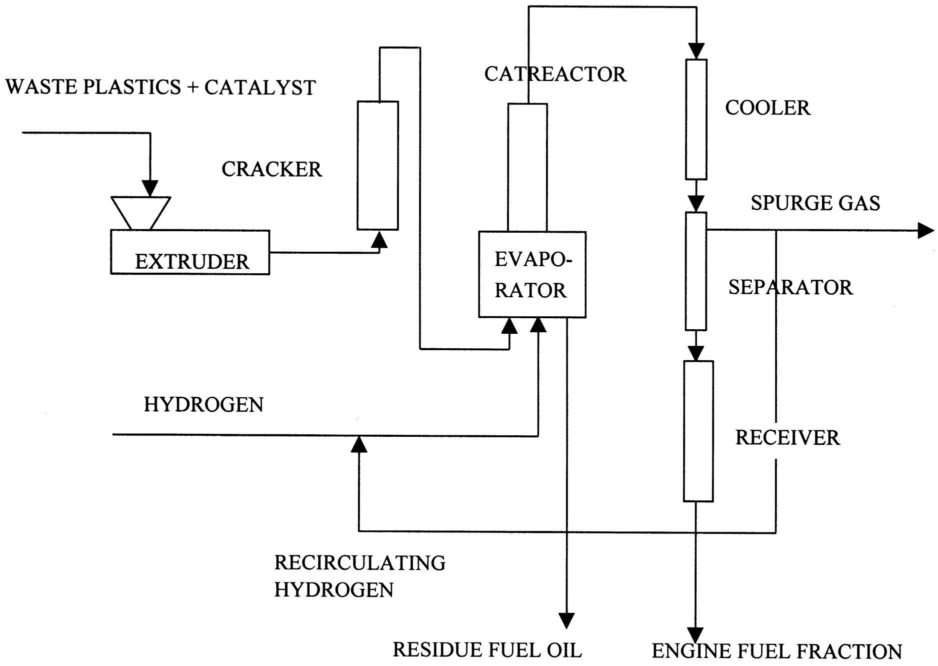

Fig. 6. Scheme of processing of waste plastics with hydrogenation of fuel fraction.

4. Conclusions

- The optimum thermal cracking temperature of waste polyolefines is 410–30°C; in the case of catalytic cracking or hydrocracking lower process temperature can be used, ca. 390, reaction time 1.5 an hour. About 90% or even higher conversion to gas and fuel fractions with b.p. < 360°C can be attained.
- In the range of catalyst content (0.3–1 wt.%) there is rather small influence of quantity of catalyst on polyolefines conversion and reaction products composition.
- The liquid fractions obtained in the presence of hydrocracking catalyst are characterised by lower boiling range and lower unsaturated hydrocarbons content in comparison to liquid fractions obtained using cracking catalyst or thermal cracking.
- Extent of catalytic depolymerization of polystyrene at similar process parameters is similar to the polyethylene one but liquid products are less unsaturated and much more aromatic.
- Physicochemical properties of the obtained products depend on waste plastics composition. Cracking or hydrocracking of polyethylene connected with hydrogenation step gives mainly paraffin fractions while in the case of polystyrene highly aromatic fraction fuel fractions.
- Continuous process of waste plastics processing for engine fuel production is presented.

References

[1] N. Shah, J. Rockwell, G.P. Huffman, Energ. Fuel 13 (1999) 832.
[2] I. Nakamura, K. Fujimoto, Catal. Today 27 (1996) 175.
[3] G. de la Puente, J.M. Arandes, U. Sedram, Ind. Eng. Chem. Res. 36 (1997) 4350.
[4] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Appl. Catal. B 2 (2–3) (1993) 153.
[5] W. Ding, J. Laing, L.L. Andersen, Fuel Process. Technol. 51 (1997) 47.
[6] Z. Zhibo, S. Nishio, Y. Moriaka, A. Ueno, H. Ohkita, Y. Tochihara, Y. Mizushima, N. Kakuta, Catal. Today 29 (1996) 303.
[7] Y. Uemichi, M. Hattori, T. Itoh, J. Nakamura, M. Sugioka, Ind. Eng. Chem. Res. 37 (1998) 867.
[8] H.S. Joo, J.A. Guin, Fuel Process. Technol. 57 (1998) 25.
[9] J. Walendziewski, M. Steininger, Pol. Pat. Appl. 336 733 (1999).