Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts
Effect of polymer to catalyst ratio/acidity content

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Abstract

The catalytic degradation of polyethylene over two commercial cracking catalysts, containing 20% and 40% ultrastable Y zeolite, respectively, was studied in a semi-batch reactor. More specifically, the effect of the polymer to catalyst ratio – expressed as the acidity content of the polymer/catalyst system – was studied on the formation of liquid hydrocarbons. After a sharp increase at small values, the liquid yield seemed to have a negative correlation to the acidity content, showing a maximum at acidity values around 7% of pure US-Y. Regarding the boiling point distribution of the liquid fraction in systems with higher content of active catalyst, a shift was generally observed towards lighter products. Comparing liquid samples during the same experiment, later samples contained heavier components with the exception of the system with the smallest US-Y content of this study.
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1. Introduction

The huge amount of waste plastics that resulted from the dramatic increase in polymer production gives rise to serious environmental concerns, as plastic does not degrade and remains in municipal refuse tips for decades. Plastic waste being more voluminous than the organic waste takes up a lot of landfill space that is becoming scarce and expensive. Incineration is not an acceptable solution to the problem, as toxic gases are produced and a solid waste problem becomes an air pollution. The only sustainable solution is polymer recycling. Between various polymer recycling methods, thermal and/or catalytic degradation of plastic waste to fuel show the highest potential for a successful future commercial process [1–5], especially as plastic waste can be considered as a cheap source of raw materials in times of accelerated depletion of natural resources. Catalytic degradation of plastic waste of-

fers considerable advantages as compared to pure thermal degradation, as the latter demands relatively high temperatures and its products require further processing for their quality to be upgraded. Catalytic degradation occurs at considerably lower temperatures [1] and forms hydrocarbons in the range of motor engine fuel [1–5], eliminating the necessity of further processing. In such a recycling process, the most valuable product is obviously liquid fuel. Although gaseous products are useful too, as their burning can contribute to the energy demand of an endothermic polymer cracking process, excess gas production is not desirable. Gaseous products are considered of low value because of their transportation costs. Consequently, the target of a commercially viable recycling process should be an increase of the liquid product yield.

For such a catalytic process mainly zeolite-based catalysts [1,2,5,6,9–16] have been used, as well as silica–alumina [6–9], clay-based catalysts [3–5] and MCM-type mesoporous materials [17]. In the search of further catalysts for improving the yield to liquid fuel in the plastic catalytic cracking, we recently introduced two commercial cracking catalysts,

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containing 20% and 40% ultrastable Y zeolite (US-Y), respectively [5]. This study has shown the suitability of commercial cracking catalysts for such a polymer degradation process. Furthermore, containing only a small amount of zeolite, cracking catalysts are less acidic and produce, therefore, more liquid hydrocarbons than their parent zeolite [5]. The test of commercial cracking catalysts is important as one of the options of commercialising this polymer recycling method is to co-feed polymer waste to existing refinery crackers [11,14–16].

This paper reports on the results of a further study of polymer degradation over commercial cracking catalysts. More specifically it reports on the effect of the acidity content, indicative of the polymer to catalyst ratio, on the yield of liquid products and their quality, as measured by the boiling point distribution.

2. Experimental

2.1. Materials

The model polymer feed was unstabilised linear low-density polyethylene (lldPE) in a powder form (average particle size, 100 μm), kindly provided by BASF AG with a density of 0.928 g/cm^3 and an average molar mass of 117 kg/mol.

The catalyst samples used were two commercial cracking catalysts, named cracking catalyst 1 and cracking catalyst 2, containing 20% and 40% US-Y, respectively (average particle size, 100 μm) kindly provided by AKZO-NOBEL.

Ammonia temperature-programmed desorption (TPD) on a Micromeritics ASAP 2910 Chemisorption equipment (ca. 100 mg of sample at 10 K/min from 373 to 1073 K) was used to estimate the acidity of the individual catalyst samples. The measured acidities did not correspond to the provided US-Y content information obviously due to the contribution from the other catalyst ingredients. The acidity values are listed in Fig. 1, where the TPD runs of the three samples are plotted.

2.2. Experimental equipment

The experimental apparatus for catalytic degradation of lldPE consisted of a semi-batch Pyrex reactor in which the
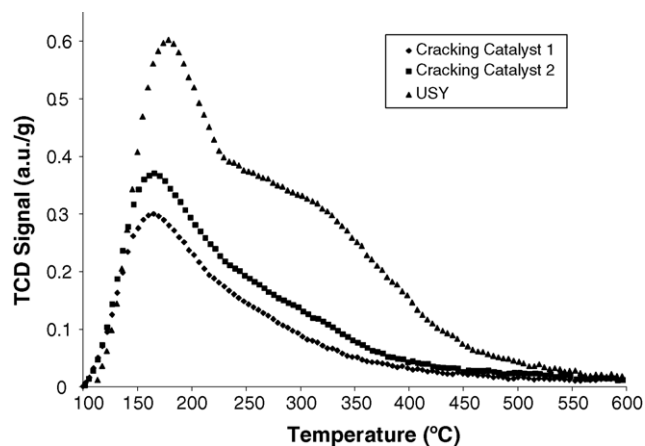

Fig. 1. Temperature-programmed desorption of NH$_3$ over US-Y and the commercial cracking catalyst samples of this study (10 K/min from 37 to 1073 K).

reaction took place, heated by two semi-circle infrared heating elements for fast heating, connected to a programmable temperature controller. Prior to the reaction, the reactor was purged with nitrogen in order to remove any oxygen. Polymer mixed with catalyst was charged into the reactor at the beginning and the reactor was heated up. During the experimental run the reactor was purged with nitrogen (50 ml$_N$/min determined by a mass flow controller) in order to remove the volatile reaction products from the reactor. The polymer to catalyst ratio was varied, as its effect on the liquid yield was the objective of the study. The mass ratios of the polymer to catalyst, the US-Y fractions in the polymer/catalyst system as well as the acidity content are given in Table 1. The acidity content was expressed as fraction of the US-Y acidity on its own and was calculated as:

$$\text{Acidity content} = \frac{(\text{Catalyst content\%}) \times (\text{Catalyst acidity})}{\text{USY acidity}}.$$

According to this, 100% corresponds to a pure US-Y system in the absence of any polymer. The overall mass of polymer and catalyst was kept between 2.5 and 3 g.

A constant set-point for the controller temperature was used throughout the 25 min of the experiment, which resulted in the following reactor temperature profiles (Fig. 2). In the

Table 1
Polymer to catalyst mass ratio during catalytic cracking of lldPE over-cracking catalyst 1 (20% US-Y) and catalyst 2 (40% US-Y)

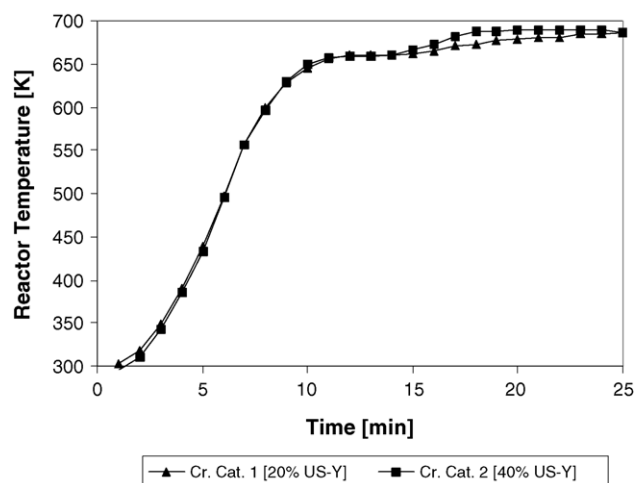| Polymer to catalyst mass ratio	Content of cracking catalyst (%)	US-Y catalyst content (%)	Acidity content (%) (100% = pure US-Y/no pol)	Polymer mass (g)	Catalyst mass (g)	Total mass (g)
Cracking catalyst 1 (20% US-Y) acidity: 36% of US-Y						
1:1	50.0	10.0	17.9	1.5	1.5	3.00
2:1	33.3	6.7	11.9	2.01	1.01	3.02
4:1	20.0	4.0	7.2	2.05	0.51	2.56
6:1 (exact ratio = 5.9:1)	14.5	2.9	5.1	2.13	0.36	2.49
Cracking catalyst 2 (40% US-Y) acidity: 48% of US-Y						
1:1	50.0	20.0	24.2	1.52	1.52	3.04
2:1	33.3	13.3	16.1	2.04	1.02	3.06
4:1	20.0	8.0	9.7	2.26	0.56	2.82

Fig. 2. Temperature profiles during polymer degradation over commercial cracking catalysts 1 and 2.

first 10 min, a linear reactor temperature increase was obtained to a temperature of ca. 650 K, with a subsequent slow rise to ca. 690 K during the remaining 15 min of the experimental runs.

Liquid products were collected in the condensers placed in an ice bath (273 K) and analysed by GC equipped with a flame ionisation detector (FID) using a J&W Scientific DB-Petro capillary column (100 m × 0.25 mm × 0.5 μm). Using a two-way valve, collection of samples at various reaction times and temperatures was possible. Four samples were collected during all experiments, one during the temperature increase stage in the first 10 min, where the real collection time was between the 5th and 10th min as no liquid was formed during the first 5 min, and another three in 5-min intervals afterwards (10–15, 15–20, 20–25 min).

2.3. Experimental calculations in the semi-batch reactor equipment

The conversion to volatile products was calculated as the fraction of the initial mass of polymer reacted to form the volatile products. The selectivity to liquid products was calculated as the mass of liquid collected divided by the mass of reacted polymer. The yield to liquid products was calculated as the mass of liquid collected divided by the initial amount of polymer and represents the fraction of original polymer converted to liquid products. Liquid yield values were estimated at various reaction times, as the use of a two-way valve enabled the collection of various liquid samples during the reaction. The coke yield was calculated by dividing the mass of un-volatilised polymer on the catalysts by the original mass of polymer and hence: coke yield = 1 − conversion. The un-volatilised polymer represented the coke formed on the catalyst. Visual inspection at the end of experimental runs revealed the coked catalysts to be the only phase present in the reactor and no remnant polymer mass. The coke concentration was calculated by dividing the mass of coke by the mass of dried catalyst.

The boiling point distribution of each liquid fraction was used to represent the liquid product distribution. That was possible as the employed non-polar capillary column separated the components of the liquid fractions according to their volatility/boiling point. A calibration mixture containing normal alkanes, pentane to eicosane (C_5–C_{20}) was prepared and used to assign each retention time observed from the chromatogram to a boiling point. This enabled the whole analysis of a sample to be divided into intervals between the boiling points of the normal alkanes of the calibration mixture [5]. The mass fraction corresponding to each interval was calculated from the sum of the area fractions of all components in this interval. To each interval the probability density function value was then calculated as being equal to the mass fraction of this interval divided by the temperature interval width ΔT. Hence the probability density function is expressed as %/K. In the graphs of the boiling point distribution each interval is represented by its middle value. All components with retention times smaller than this of n-pentane were assigned to a group corresponding to the boiling point interval between n-butane and n-pentane (272.7–309.2 K).

Table 2
Conversion, liquid yield, liquid selectivity, coke yield and coke concentration during catalytic cracking of lldPE over-cracking catalyst 1 (20% US-Y) and catalyst 2 (40% US-Y)

Polymer to catalyst ratio	Conversion (%)	Yield to liquid product (%)	Selectivity to liquid product (%)	Coke yield (%)	Coke concentration (%)
Cracking catalyst 1 (20% US-Y) acidity: 36% of US-Y					
1:1	98	66	67	2	2
2:1	99	76	77	1	2
4:1	99	89	90	1	4
6:1	99	73	74	1	6
Cracking catalyst 2 (40% US-Y) acidity: 48% of US-Y					
1:1	94	41	44	6	6
2:1	95	66	69	5	10
4:1	93	78	84	7	28

3. Results and discussion

3.1. Conversion, yield to liquid products, liquid selectivity, coke yield and coke concentration

The overall conversion, liquid yield and selectivity, as well as coke yield and concentration obtained over-cracking catalysts 1 and 2 are summarised in Table 2. Cracking catalyst 1 could fully degrade the polymer samples in all cases, even at low values of overall content of the active zeolite US-Y. No polymer remnants were observed and coke formed on catalyst was the only form of the polymer not converted to volatile products. In terms of overall liquid yield and selectivity, a maximum was observed around a ratio 4:1. In the same case of 4:1, the liquid yield was very close to 90%, an exceptionally high value. The low coke yields reflect upon the high conversion values reached. However, coke concentrations, the ratio of formed coke to catalyst mass, were higher, as higher polymer to catalyst ratios were applied. High conversion values were obtained also with cracking catalyst 2 at all different polymer to catalyst ratios studied. Once again, all conversion values were above 90%. The liquid yields and selectivities were not so high when compared to cracking catalyst 1, but ratio 4:1 produced the highest values (78% and 84%, respectively). Stronger coke formation was observed with cracking catalyst 2 containing 40% of the active US-Y than the cracking catalyst 1, reflecting also upon the conversion values. Obviously the higher content of the strongly acidic US-Y enhanced coking, that is a reaction catalysed by strong acid sites [18].

The liquid yield versus time graph is presented in Fig. 3 for different polymer to catalyst ratios for commercial cracking catalyst 1 for clearer interpretation of results. It clearly indicates that ratio of polymer to catalyst 4:1 produces a higher liquid yield (89%) as compared to the rest, as well as higher liquid yield values during the whole experimental run. On a careful inspection of the results a clear pattern emerges for the formation of liquid products. At low catalyst contents the liquid yield keeps increasing during the whole reaction
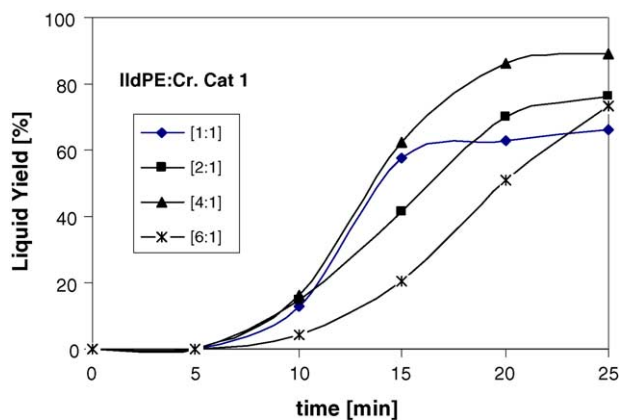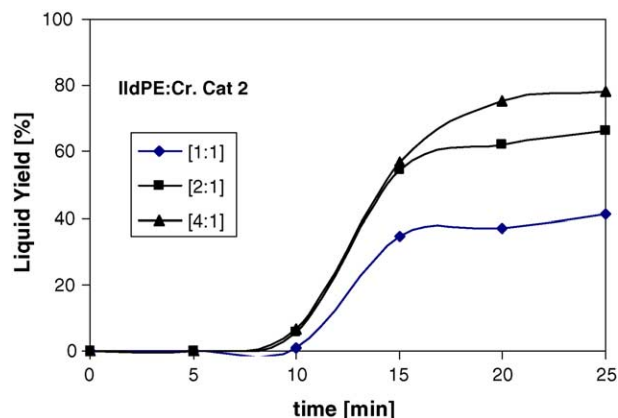
Fig. 4. Liquid yield vs. time during lldPE degradation over-cracking catalyst 2 (40% US-Y) at different polymer to catalyst ratios.

time. As the fraction of catalyst in the polymer/catalyst mixture increases the liquid yield curve levels off, resembling the behaviour over commercial cracking catalyst 2 (Fig. 4). Over-cracking catalyst 2, a decrease of the liquid yield is observed with the catalyst content for all reaction times.

Figs. 3 and 4 suggest that there might exist a maximum above which the addition of more catalyst to the polymer has an adverse effect on the liquid yield. In order to examine this, the liquid yield was plotted against the acidity content in the polymer–catalyst system. The acidity content in this plot was expressed as the fraction of the US-Y acidity on its own, as explained in Section 2. This means that 100% acidity corresponds to a pure US-Y system in the absence of any polymer. The plot containing data from both cracking catalysts is presented in Fig. 5. We included the origin in the graph as no liquid was formed in the absence of catalyst [5] while less than 5% of the polymer was converted. With the addition of small amount of active catalyst (2.9% US-Y, 6:1 lldPE: cracking catalyst 1), liquid is formed in significant amount and with almost the same rate throughout the whole reaction time. Obviously the amount of catalyst is not sufficient to convert the polymer fast enough resulting in a comparable liquid formation rate during the whole experiment. With the addition of some more active catalyst (4.0% US-Y, 4:1 lldPE: cracking catalyst 1), liquid formation increases considerably

Fig. 3. Liquid yield vs. time during lldPE degradation over-cracking catalyst 1 (20% US-Y) at different polymer to catalyst ratios.
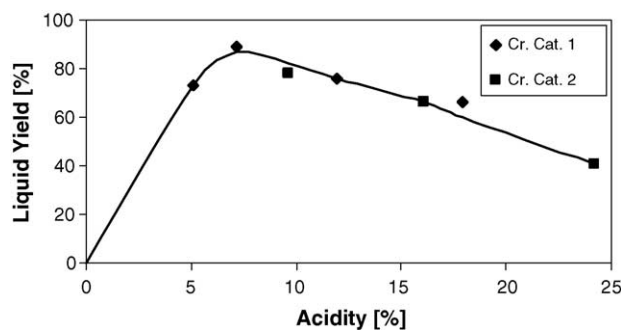
Fig. 5. Overall liquid yield vs. acidity over both commercial cracking catalysts.

so that later on in the experiment the liquid formation rate levels off, since obviously most of the plastic has been converted. Addition of more active catalyst does lead to over-cracking into smaller molecules, which are collected in the gaseous product fraction. As a result, a maximum is formed around 7% of acidity in the liquid yield versus acidity curve (Fig. 5). Small deviations between cracking catalysts 1 and 2 data might be due to some minor different characteristics of the two samples, but the overall trend of liquid formation shows a drastic increase at small active catalyst contents, and hence low acid sites concentration with a subsequent gradual decrease at higher content values. The same pattern showing a maximum is apparent at various reaction times (Fig. 6), where it becomes obvious also that the drastic increase in liquid yield takes place between 10 and 15 min, apart from the systems with low percentages of US-Y content.

3.2. Product distribution

From the experimental runs with analyses of liquid samples at different reaction times, the tendency has been confirmed [4,5] that the liquid fractions formed at later reaction times have a higher average boiling point. Obviously earlier samples formed at lower temperatures are expected to contain a higher proportion of lower boiling components. Reactions at lower temperature on the other side are expected to lead into scission of smaller chain fragments, while larger fragments that demand higher activation energies are broken away at higher temperatures. Furthermore, solid-phase cross-linking reactions change the nature of the polymer reactant, making it more difficult to degrade. A shift is observed towards less volatile hydrocarbons from the first collected liquid sample to later samples, see for example Fig. 7 for the case of cracking catalyst 1 at polymer to catalyst ratio 4:1 (4% US-Y content). However, for the same catalyst at 6:1 ratio (2.7% US-Y), the picture reverses (Fig. 8). Clearly the first collected sample contains a higher fraction of components with a boiling point lower than this of normal octane and correspondingly a higher
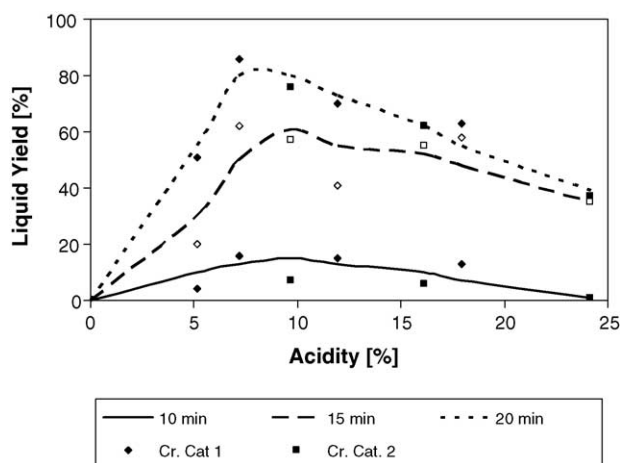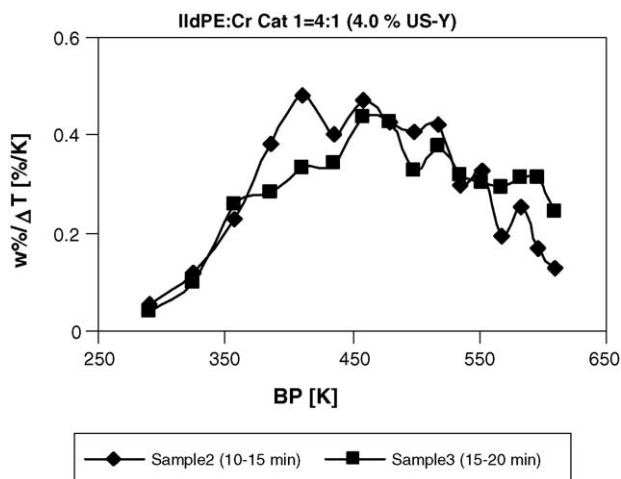

Fig. 7. Boiling point distribution of liquid samples formed during catalytic degradation of lldPE over-cracking catalyst 1 (20% US-Y) at polymer to catalyst ratio 4:1; overall US-Y content in polymer–catalyst system: 4%, acidity 7.2%.

fraction of heavy components than the second collected liquid sample. Although this trend is reversed, it is in agreement with the fact that at this lowest value of acidity content the liquid yield is lower than at the next value. The concentration of acid sites is so low that the catalyst system needs longer time for the degradation reaction to progress. While at other polymer to catalyst ratios, i.e. higher acidity, all the polymer mass seems to undergo cracking reactions, at 2.7% US-Y content obviously not all the polymer mass participates in degradation reactions possibly due to not being in contact with the catalyst. While the second liquid fraction is usually formed from the conversion of further reactions of already partially degraded polymer, it seems that the volatile components of the second collected sample at the system with 2.7% US-Y are formed directly from conversion of undegraded polymer.

Fig. 6. Liquid yield vs. acidity over both commercial cracking catalysts at different reaction times.
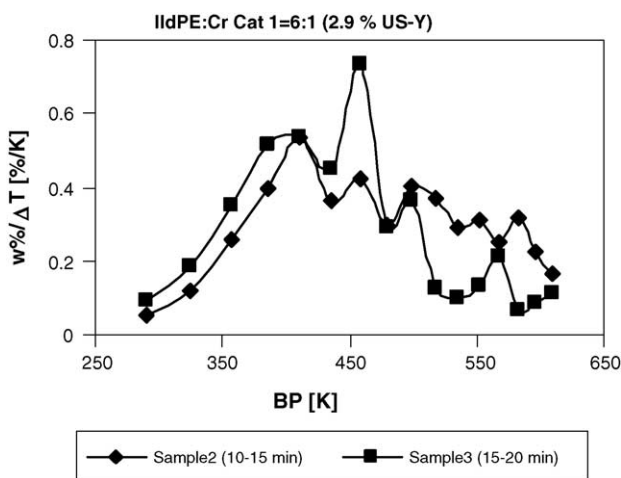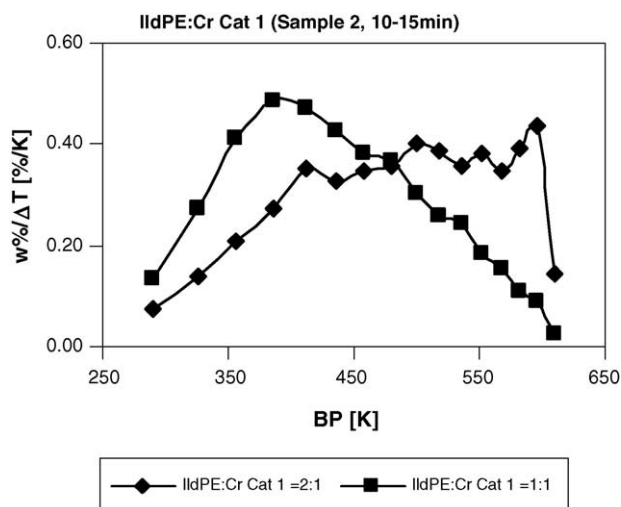

Fig. 8. Boiling point distribution of liquid samples formed during catalytic degradation of lldPE over-cracking catalyst 1 (20% US-Y) at polymer to catalyst ratio 6:1; overall US-Y content in polymer–catalyst system: 2.7%, acidity 5.1%.

Fig. 9. Boiling point distribution of liquid samples formed during catalytic degradation of lldPE over-cracking catalyst 1 (20% US-Y) at polymer to catalyst ratio 2:1 (overall US-Y content in polymer–catalyst system: 6.7%, acidity 11.9%) and ratio 1:1 (overall US-Y content in polymer–catalyst system: 10%, acidity 17.9%).

Comparing the boiling point distribution of liquid fractions formed over-cracking catalyst 1 at 2:1 polymer to catalyst ratio and 1:1 ratio, Fig. 9, it is obvious that the higher acidity in the second case causes a shift towards more volatile components. Due to the lower acidity of the first system the liquid formed contained a lower amount of light hydrocarbons and a higher amount of heavy hydrocarbons than the liquid formed in the second case. A better inspection of the same comparison for cracking catalyst 2 reveals a slightly different picture (Fig. 10). A simple grouping of the liquid products into light and heavy does not describe the full picture. Although the liquid fraction of the 1:1 system contains
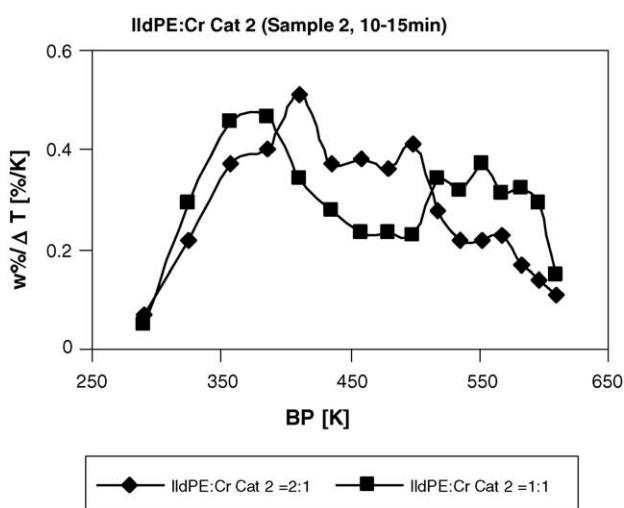
again more light components, it also contains more heavy components, but considerably less middle boiling point components than the 2:1 system does. It seems that in the 1:1 case (20% overall US-Y content) the low boiling point components are predominantly formed from further cracking of middle point hydrocarbons rather than the decomposition of heavy ones. These initial results indicate that heavy components break down into middle volatility components, which undergo further cracking into light hydrocarbons. The results reported here are only these of preliminary studies. Further more detailed studies are needed in order for the exact nature of secondary cracking reactions to be revealed.

4. Conclusions

A clear trend of liquid hydrocarbon formation was observed with the acidity content during the catalytic degradation of polyethylene over the commercial cracking catalysts. An initial sharp increase of the liquid yield at low US-Y content – low acidity content – is followed by a gradual decline at higher values. This results in a maximum of liquid yield at acidity values around 7% as compared with a pure US-Y system in the absence of the polymer. At low acidity values, below the maximum, the amount of acid sites is not enough for the conversion of the whole polymer mass, while above the maximum point stronger acidity leads to over-cracking and hence more gaseous products.

Further detailed systematic studies are suggested in order to illuminate the pattern of secondary reactions taking place and establish an overall reaction scheme.

Acknowledgements

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Fig. 10. Boiling point distribution of liquid samples formed during catalytic degradation of lldPE over-cracking catalyst 2 (40% US-Y) at polymer to catalyst ratio 2:1 (overall US-Y content in polymer–catalyst system: 13.3%, acidity 16.1%) and ratio 1:1 (overall US-Y content in polymer–catalyst system: 20%, acidity 24.2%).

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