

HYDROCRACKING OF WASTE PLASTICS TO CLEAN LIQUID FUELS

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Keywords: hydrocracking, waste plastics, liquid fuels

ABSTRACT

Recycling of waste plastics and other packaging materials is becoming more necessary since they represent a readily available source of fuels and/or chemicals and a growing disposal problem. One way of accomplishing such recycling is to convert these waste polymers into transportation fuels by thermal and/or catalytic processing. In recent work thermal processing was found to be easily accomplished. However, the products were not of sufficiently high quality to be used as transportation fuels without extensive upgrading. Waste materials from the U.S. (American Plastics Council) and Germany (Duales System Deutschland or DSD) were processed by hydrocracking. Commercial catalysts, KC-2001 and KC-2600 were used in hydrocracking experiments using 27 ml tubing reactors. Effects of reaction temperature, hydrogen pressure, and reaction time on product yields and quality were studied. The liquid products were subjected to detailed analysis by GC, GC/MS, and TG/MS. Possible reaction mechanisms will be proposed based on the analytical data. Other bifunctional catalysts developed in our laboratory were also tested and results will be compared with those obtained using the mentioned commercial catalysts.

INTRODUCTION

Conversion of waste plastic to clean liquid fuels has been widely studied all over the world recently [1,2]. Most bench scale and pilot plant studies employed two-stage processes, i.e., in the first stage, plastic is thermally degraded to crude oil-like liquid products, and the liquids are subjected to further catalytic cracking to produce gasoline-like products in the second stage. This process may be more costly than a single stage processing, i.e., direct conversion of waste plastic to gasoline-like products [3]. The challenge of the latter is to utilize high efficiency catalysts. Pure polymers, such as high density polyethylene, polypropylene, polystyrene, etc., are different than waste plastics which contain some nitrogen, sulfur, and even chlorine, as well as impurities. These compounds are believed to be poisonous to some catalysts which were effective in cracking pure polymers. Therefore, a catalyst with not only hydrocracking-hydrogenation ability, but also hydrodenitrogenation-hydrodesulfurization function is needed for directly converting waste plastics to clean liquid fuels.

In this study, two commercial hydrocracking catalysts (KC-2001 and KC-2600), obtained from Akzo Nobel Chemical, Inc., were used for hydrocracking two different kinds of waste plastics; one from the American Plastics Council (APC plastic) and the other from Germany's Duales System Deutschland (DSD plastic). A catalyst (Ni supported on a mixture of zeolite and silica-alumina) made in this lab was also tested and the results are compared.

EXPERIMENTAL

APC plastic, obtained from the American Plastics Council, was ground to -8 mesh. Detailed analyses of this plastic are listed elsewhere [4]. DSD plastic, obtained from Germany's Duales System Deutschland, was used as received except for drying before reaction. The results of ultimate and proximate analyses are listed in Table 1, whereas the results of ash analyses are listed in Table 2 [5]. HZSM-5 and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (with 13% Al_2O_3 content), were purchased from United Catalysts Inc. and Aldrich Chemical Company, respectively. The average pore size and surface area of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ were 65 Å and 475 m^2/g respectively; while those of the HZSM-5 were 6.2 Å and ca. 200 m^2/g respectively. The metal salts, nickel (II) nitrate hexahydrate was obtained from Aldrich Chemical Company. KC-2001 and KC-2600 were obtained from Akzo Nobel Chemicals, Inc., whereas as Ni/HSiAl (HSiAl is a mixture of four parts by weight of silica-alumina and one part by weight of HZSM-5) was prepared in this lab. All three catalysts were presulfided before reaction [6].

Hydrocracking reactions of DSD and APC plastics were carried out in a 27 ml tubing reactor at 375 to 480°C for 60 minutes. Typically, 2 g of plastic and a calculated amount of presulfided catalyst, if any, were fed into the reactor, which was then closed, purged with nitrogen,

and then pressurized with hydrogen to the desired initial pressure, usually 1000 psig. The reactor was then immersed into a preheated fluidized sand bath and reached the desired reaction temperature within 3 to 4 minutes. The mixing of reactants and catalyst particles was achieved by horizontal shaking of the reactor at 160 rpm. Detailed reaction procedure and definitions of yields have been reported elsewhere [7].

The gases obtained from the first stage were analyzed by a flame ionization detector by gas chromatography (HP-5890II) using a column packed with HayeSep Q. The liquid products were analyzed by GC/MS using a 30-m long DB-5 capillary column. The boiling point distribution of the liquid products were determined by simulated distillation according to ASTM D 2887-89 and D5307-92. The analysis was performed on a HP-5890 series II gas chromatograph, using a Petrocol B column (6 inches long and 0.125 inches outside diameter).

RESULTS AND DISCUSSION

Hydrocracking of APC Plastic. Some 99% conversion was obtained when APC plastic was noncatalytically degraded at 435°C or at 480°C [7,8]. However, the quality of oil products obtained was far below that of commercial premium gasoline. Hydrocracking catalysts, KC-2600 and Ni/HSiAl, were effective for degradation of APC plastic at 375°C (Figure 1). The conversion was markedly increased in the presence of the mentioned catalysts. Figure 2 shows the GC/MS profile of oil products obtained over KC-2600. The oil contains mostly isoparaffins, some n-paraffins, and small amounts of aromatics as well as cycloparaffins. This indicates that KC-2600 does have hydrocracking and hydroisomerization ability. The oil was also subjected to elemental analysis and no nitrogen and sulfur was detected, suggesting HDN and HDS ability of the catalyst. [6].

Hydrocracking of DSD Plastic. DSD plastic can be hydrocracked thermally to produce gaseous and liquid products. Figure 3 shows the effect of reaction temperature on thermal hydrocracking of this plastic. The conversion was not a function of temperature in the temperature range of 450 to 480°C, although conversion increased markedly with temperature increasing from 370 to 450°C. Different from the APC plastic, this DSD plastic contained about 4.4% ash. Therefore, the maximum conversion should be about 95% and this value was reached at temperatures higher than 450°C. The maximum yield liquid was also obtained at 450°C, indicating further thermal cracking to form smaller size molecules, such as gases, at temperature higher than 450°C. It is reasonable to suggest that 450°C is the optimum temperature for thermally converting DSD plastic to liquid products.

The oil products obtained at 430, 450, and 480°C were subjected to simulated distillation analyses and the results are shown in Figure 4. Not surprisingly, the oil obtained at higher reaction temperatures was lighter than that obtained at lower temperature. The liquids need further treatment for use as transportation fuels, such as gasoline.

The effects of catalysts on hydrocracking of DSD plastic are shown in Table 3. At 375°C, only about 10% conversion was achieved for thermal reaction, however, the conversion reached 66.7% when 40% KC-2001 was added (Figure 3 and Table 3). The effects of the catalysts decreased in the order: KC-2001 > Ni/HSiAl > KC-2600. It is noteworthy that conversion of APC plastic reached over 90% in the presence of KC-2600 or Ni/HSiAl (Figure 1), whereas only 30-50% conversion were obtained for DSD plastic at the same reaction conditions (Table 3). The analyses showed that the main difference between APC plastic and DSD plastic was that the latter contained some chlorine, more ash, and some waste paper (Table 1). These materials may have some negative effects on these catalysts at the conditions used. The conversion of DSD plastic was enhanced when temperature was increased to 400°C and the amount of catalyst was decreased to 20% (Table 3). Some 80% conversion was obtained over 20% KC-2001 at 400°C. Additional experiments showed that about 94% DSD plastic was converted to gaseous and liquid products over 40% KC-2001 at 400°C. This indicates that KC-2001 may be a suitable catalyst for hydrocracking of DSD plastic to liquid fuels.

CONCLUSIONS

APC plastic can be converted totally to liquids and gases at 375°C in the presence of a hydrocracking catalyst, Ni/HSiAl or KC-2600. The quality of the liquid products obtained was close to that of a commercial premium gasoline. Catalytic hydrocracking of DSD plastic at the same conditions was found to be more difficult than that of APC plastic. This may be due to the negative effects of some impurities contained in DSD plastic, such as chlorine, ash, and paper. At 400°C, DSD plastic can be nearly totally converted to gaseous and liquid products with 40% KC-2001 catalyst. The products obtained will be analyzed further.

Thermal hydrocracking of DSD plastic is feasible, and the optimum reaction temperature was found to be 450°C. At this condition, DSD plastic can be totally converted and the yield of liquid products can reach as high as some 60%.

ACKNOWLEDGMENT

The authors gratefully acknowledge the funding support from the U.S. Department of Energy through the Consortium for Fossil Fuel Liquefaction Science.

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Table 1. Proximate and Ultimate Analyses of DSD Plastic

	wt%
Proximate analysis	
Moisture	0.16
Ash	4.44
Volatile matter	93.77
Fixed carbon	1.08
Ultimate analysis	
Carbon	78.96
Hydrogen	13.5
Nitrogen	0.67
Chlorine	1.26
Sulfur	0.08

Table 2. Ash Analyses of DSD Plastic (by ICP)

	wt%
Al	10.0
As	<40 ppm
Be	<1 ppm
Ca	13.0
Cd	<1 ppm
Co	26 ppm
Cr	0.08
Cu	0.02
Fe	3.5
K	1.85
Mg	2.05
Mn	0.08
Mo	40 ppm
Na	3.9
Ni	0.01
Pb	0.01
Se	<40 ppm
Si	18.0
Ti	12.8
V	21 ppm
Zn	0.43

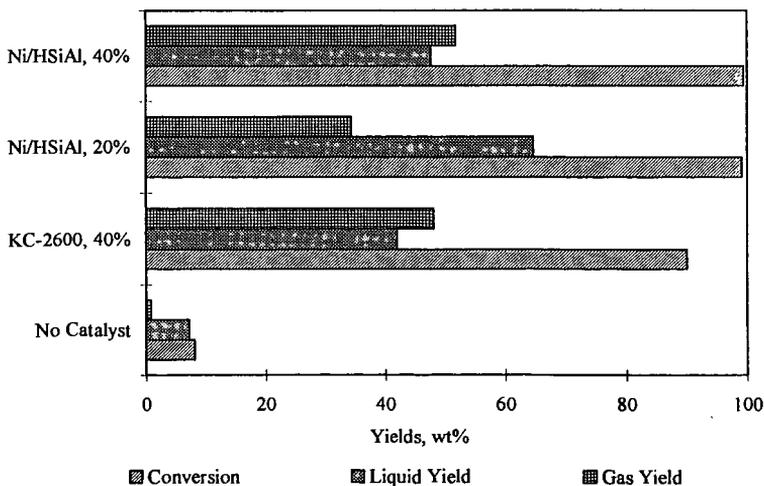


Figure 1. Results of degradation of APC plastic in a 27 ml tubing reactor at 375°C, 1000 psig H₂ (initial), for a reaction time of 1 h with the indicated catalysts.

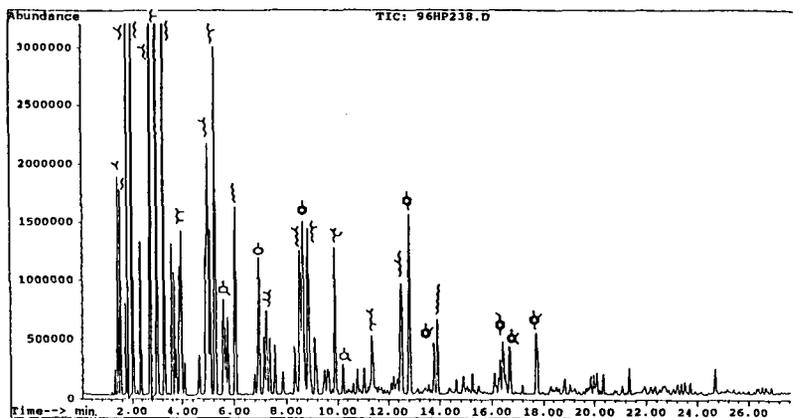


Figure 2. GC/MS analyses of the oil products obtained from hydrocracking of APC plastic in a 27 ml tubing reactor at 375°C, 1000 psig H₂ (initial), for a reaction time of 1 h with 40% KC-2600

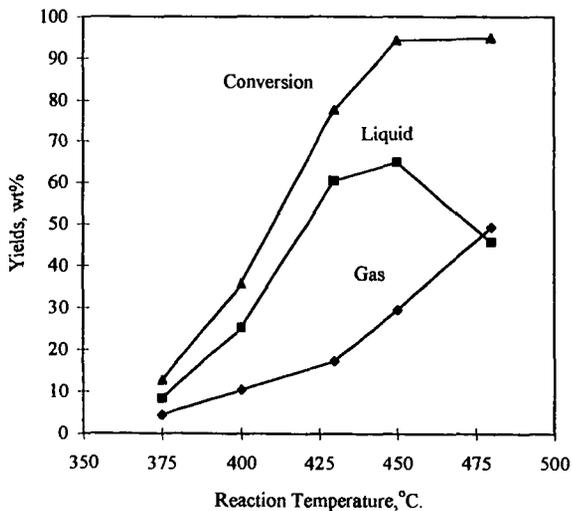


Figure 3. Effect of reaction temperature on thermal hydrocracking of DSD plastic (reaction conditions: 27 ml tubing reactor, 1000 psig H₂ (initial), 60 minutes, 160 rpm)

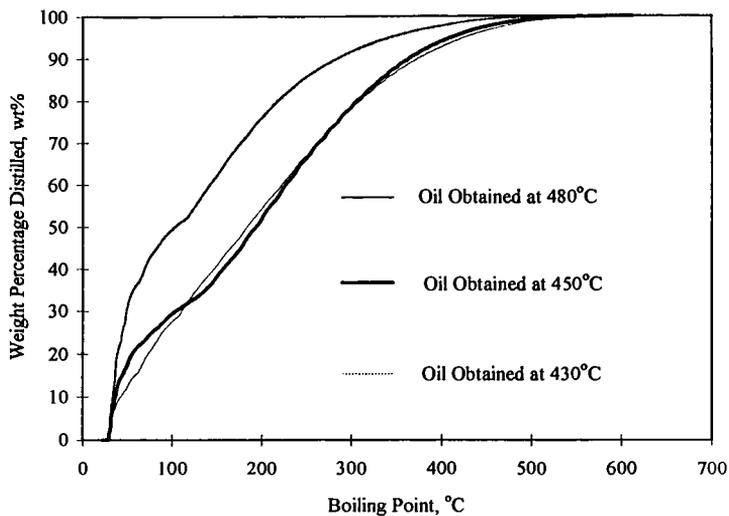


Figure 4. Boiling point distribution of oils obtained from thermal hydrocracking of DSD plastic at 1000 psig H₂ (initial), 60 minutes

Table 3. Results of Catalytic Hydrocracking of DSD Plastic in a 27 ml Tubing Reactor at 1000 psig H₂ (initial), for a Reaction Time of 60 Minutes.

Catalyst	Gas Yield, wt%	Oil Yield ^a , wt%	Conversion ^b , wt%
375°C			
KC-2001 ^c , 40%	35.7	31.0	66.7
KC-2600 ^c , 40%	10.2	20.7	30.9
Ni/HSiAl, 40%	14.8	35.1	49.9
400°C			
KC-2001 ^c , 20%	39.9	38.8	78.7
KC-2600 ^c , 20%	15.2	48.2	63.4
Ni/HSiAl, 20%	20.0	45.5	65.5

^a n-pentane soluble;

^b Conversion (wt%) = 100(1-weight of pentane insolubles/weight of feed);

^c Catalysts, obtained from Akzo Nobel Chemicals Inc., may contain NiMo/Al₂O₃ and/or NiMo/zeolite.