

COPROCESSING OF WASTE PLASTICS WITH COAL AND PETROLEUM RESID USING DIFFERENT CATALYSTS

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Keywords: Coprocessing, petroleum resid, coal, waste plastics

INTRODUCTION

Waste plastics are a source of hydrocarbons that are currently not being used effectively. Only ~2% of the plastics are being recycled (Smith, 1995), and the remainder is being disposed of in landfills. Waste plastics are produced from petroleum and are composed primarily of hydrocarbons but also contain some antioxidants and colorants (Leidner, 1981). A number of problems are associated with the recycling effort, including convincing consumer households of the necessity to recycle, separating the waste plastics effectively for primary recycling of the plastic back to the monomer, and having sufficient waste plastic for processing, particularly in areas a far distance from the population centers. Tertiary recycling that results in the production of fuels and chemical feedstocks from waste plastics will provide an additional source of hydrocarbon fuels and chemical feedstocks. The addition of other hydrocarbon sources such as our most abundant U.S. hydrocarbon resource, coal, will provide a constancy of supply as well as an additional source of hydrocarbon fuels and feedstocks.

The direct coprocessing of coal and waste plastics is difficult because of chemical and processing incompatibility of the two materials (Luo and Curtis, 1996 a, 1996 b; Joo and Curtis, 1995, 1996). Typical household plastics waste consists of ~ 63% polyolefins (high and low density polyethylene (HDPE, LDPE)), 11% polypropylene, ~11% polystyrene, ~7% PET and 7% (Erwin and Henley, 1990), causing the wastes to be highly aliphatic. By contrast, coal is ~70% aromatic. These differences in chemistry result in the two materials being incompatible. Joo and Curtis (1996) have shown that heavy petroleum resid acts as an effective bridging solvent that when added to coal and waste plastics provides a medium for their mutual dissolution (Joo and Curtis, 1995, 1996).

The current research evaluated the effect of three different catalysts on the conversion and product distributions obtained from the coprocessing of coal, heavy petroleum resid, and waste plastics. The plastic used in this study was LDPE since it and its higher density form has been shown to be especially difficult to coprocess with coal (Luo and Curtis, 1996a). A hydrogenation catalyst with some hydrocracking activity is needed to convert coal and upgrade coal liquids and petroleum resid and a hydrocracking catalyst is required to break apart the bonds and make shorter chains of LDPE. Therefore, three different catalysts having these selectivities were employed in this study: presulfided NiMo/Al₂O₃, presulfided NiMo/zeolite, and Zeolyst Z-753, a hydrocracking catalyst. The addition of 10 wt % hydrocracking catalyst Z-732 to presulfided NiMo/Al₂O₃ was also examined to determine if adding some hydrocracking capacity to the system would increase the conversion and hexane soluble production of the plastics.

EXPERIMENTAL

Materials. The model plastic, low density polyethylene (LDPE), was obtained from Aldrich Chemical Co. and used as received. Blind Canyon DECS-17 bituminous coal was used in the study and obtained from the Penn State Coal Sample Bank. The proximate analysis of the coal is 45% fixed carbon, 45% volatile matter, 6.3% ash and 3.7% moisture. The ultimate analysis of the coal is 82.1% C, 6.2% H, 0.4% S, 1.4% N, and 0.12% Cl. The resid used was Manji obtained from Amoco. The analysis of the Manji resid is 85.1% C, 10.8% H, 0.7% N, 2.6% S, 231 ppm V, 220 ppm Ni and 23 ppm Fe. The solvents used for fractionation of the reaction products were HPLC grade hexane, toluene, and tetrahydrofuran (THF) from Fisher Scientific. Hexane solubles (HXs) were dissolved in carbon disulfide (CS₂) for simulated distillation.

The catalysts tested in this study were NiMo/Al₂O₃, NiMo/zeolite, and Zeolyst Z-753. The NiMo/Al₂O₃ catalyst from Shell was composed of 2.72 wt % Ni and 13.16 wt % Mo while the NiMo/Zeolite from Akzo was <25 wt % of molybdenum oxide and 1-10 wt % of nickel oxide with ultrastable zeolite. The Zeolyst Z-753 from Shell was composed of <60 wt % of amorphous silica, <15 wt % of tungsten oxide, <5 wt % of nickel oxide, <1 wt % of sodium oxide, and balanced alumina.

Reactions and Procedures. The reaction systems, LDPE, coal plus LDPE, and coal plus Manji plus LDPE, were studied to evaluate the activity of selected catalysts in coprocessing. Two sets of reactions were conducted: one set was performed with each of the two individual catalysts except NiMo/Al₂O₃ (Table 1) and the other with combined catalysts of NiMo/Al₂O₃ and Z-753. Reactions using a single catalyst and the same charging method as ones with combined catalyst were also performed for LDPE, coal/LDPE, and coal/Manji/LDPE systems to evaluate the effect of the catalyst combination (Table 2). For all reactions, reactants were charged at 1.0 g each for coal and polymer and 1.5 g for resid, giving resid to polymer and resid to coal ratios of 3:2 in the binary

systems and coal to resid to polymer ratios of 2:3:2 in the ternary systems. All reactions were performed using 1 wt % of powdered, presulfided NiMo/Al₂O₃ and NiMo/zeolite, and pretreated Z-753 on a total charge basis.

All reactions were performed in ~20 cm³ stainless steel tubular microreactors at 400 °C or 430 °C for 30 or 60 min with 8.3 MPa of H₂ introduced at ambient temperature. The microreactors were agitated horizontally at 450 rpm in a fluidized sand bath and were immediately quenched in water after reaction. The coal was stored in a vacuum desiccator before being used.

The procedure for presulfiding NiMo/Al₂O₃ and NiMo/zeolite began with predrying NiMo/Al₂O₃ with N₂ for one hr at 300 °C. Then, 10 vol % H₂S/H₂ gas mixture was flowed over the catalyst at 225 °C for one hr, at 315 °C for one hr, and 370 °C for two hr. In the final step N₂ was flowed N₂ at 370 °C over NiMo/Al₂O₃ for one hr and turning off the furnace to room temperature. The pretreatment procedure for Z-753 involved heating the catalyst for two hr at 204 °C, and then increasing the temperature to 538 °C for two hr. After this, it was cooled down to room temperature. During the entire procedure, the catalyst was kept under a flow of N₂. All catalysts were stored in vacuum desiccator prior to use.

The reaction products were determined by using solvent fractionation and by weighing the gaseous products. The liquid products were fractionated using a series of solvents into hexane soluble materials (HXs); toluene soluble, hexane insoluble material (TOLs); and THF soluble, toluene insoluble material (THFs), and THF insoluble material or IOM which is defined as insoluble organic matter that is moisture and ash-free. The definition for conversion used in this study is the conversion of the reactant to THF soluble material.

$$\% \text{ conversion} = \left[1 - \frac{g \text{ IOM}}{g \text{ maf total reactant}} \right] \times 100$$

The coal is a solid at room temperature and is essentially insoluble in THF; LDPE is solid at room temperature and has limited solubility in THF (3.1%), while resid is a semi-solid at room temperature and are totally soluble in THF. The boiling point distribution of HXs were analyzed using ASTM D-2887 method. Detailed procedure can be referred to in the previous work (Joo and Curtis, 1996).

RESULTS AND DISCUSSION

The investigation of coprocessing waste plastics with coal and heavy petroleum resid was performed using two different sets of reactions: a set of reactions was performed in which LDPE was reacted at four different reaction conditions with presulfided NiMo/zeolite and Z-753 catalysts, and a second set was performed in which coal, resid, and LDPE were coprocessed with the two above mentioned catalysts and presulfided NiMo/Al₂O₃, as well as with a combination of 10 wt % Z-753 with presulfided NiMo/Al₂O₃. The measures that were used to evaluate the efficacy of the catalysts were conversion of the solids to THF solubles, product distribution in terms of HXs and THFs. The boiling point distributions of the products obtained in the HXs fractions were also determined and compared for the different catalytic systems.

Individual Reaction Systems. The conversion and product distributions of LDPE reactions with the two catalysts are given in Table 1 for Z-753 and presulfided NiMo/zeolite catalysts. The reaction conditions used were 430 °C, 60 min; 430 °C, 30 min; 400 °C, 60 min; and 400 °C, 30 min. A composite of the conversion and product distribution data for the two sets of catalytic LDPE reactions is given in Figure 1. Increased reaction time and temperature resulted in higher conversions for LDPE for both the Z-753 and presulfided NiMo/zeolite catalysts. For example, with Z-753 a conversion of 35.7% was achieved at 400 °C and 30 min but increased to 94.2% when 430 °C and 60 min was used. The highest production of hexane solubles yielding 69.7% also occurred at 430 °C and 60 min. Similar LDPE reaction behavior was observed for presulfided NiMo/zeolite catalyst, although its hydrocracking activity was higher than Z-753 as evidenced by the higher conversion to gases at all reaction conditions. LDPE conversion and hexane soluble production decreased somewhat with longer reaction time at the lower temperature for both catalysts, although the gas make remained fairly constant. Recoveries were low at the highest severity condition of 430 °C which was caused by the high volatility of the reaction products.

An experimental design analysis of a 2⁴ factorial which involved 3 factors (temperature, time, and catalyst) with each two levels (400 °C and 430 °C, 30 min and 60 min, Z-753 and NiMo/zeolite), respectively, was performed for this set of experiments to determine the factor that most affected the product distribution obtained (Table 2). For production of gas, the catalyst and reaction temperature were equally strong-effect factors. The yield of hexane solubles from LDPE as well as the conversion to THF solubles, was affected by temperature as the predominant effect factor but was also affected by a two-factor interaction of reaction temperature and time. This analysis clearly demonstrated the importance in selecting reaction temperature with proper catalyst and reaction time to obtain maximum amount of desirable product from LDPE liquefaction.

Coprocessing Reactions. Individual reactions of LDPE and coprocessing reactions with coal/LDPE and coal/Manji/LDPE were performed with the three previously described catalysts and with the combination of presulfided NiMo/Al₂O₃ with 10 wt % Z-753. The conversions and product

distributions for these systems at reaction conditions of 430 °C and 60 min are given in Table 3. These high severity conditions were selected on the basis of the LDPE liquefaction results from Table 1 and of the results previous reactions containing both coal and LDPE and in some cases resid which indicated that this severity was necessary to coprocess all three materials simultaneously (Joo and Curtis, 1995, 1996; Luo and Curtis, 1996 a, b).

The catalysts directly influenced the reactivity of the LDPE liquefaction and coprocessing systems although the composition of the systems also had a strong influence on both conversion and hexane soluble yield. The LDPE conversions and product distributions obtained were directly related to the hydrocracking propensity of the catalysts. The conversions increased from 69.6% for NiMo/Al₂O₃ to 76.2% with the 10 wt% Z-753 hydrocracking catalyst present. When hydrocracking catalysts were used exclusively, the reactions with Z-753 and NiMo/zeolite produced 94.2 and 93.1% conversion, respectively. Similarly, gas production increased with hydrocracking activity with the NiMo/zeolite yielding the highest amount. The Z-753 catalyst produced the highest hexane soluble yields and conversion while the stronger hydrocracking catalyst NiMo/zeolite produced more gas and less hexane solubles.

By contrast, the coal/LDPE reactions were not influenced by catalyst type. All of the catalysts gave very similar conversions, ranging from 41.3% to 43.5%. Similarly, the amount of gas produced and hexane soluble yields were similar for all of the catalysts. The catalysts appeared to be ineffectual in the system; however, results in our laboratory have indicated that increasing the time of the LDPE/coal reaction has a significant effect on the both conversion and product distribution (Joo, 1996). Extended reaction time experiments are currently being performed to determine the effect of these catalysts on this system.

Coprocessing reactions of coal/Manji/ LDPE were influenced by the catalyst type during the 60 min reaction time as was the LDPE system. The conversion increased from 61.7% for NiMo/Al₂O₃ to 69% for 10 wt% for Z-753 in NiMo/Al₂O₃ while 100% Z-753 gave a similar conversion of 68%. The highest conversion of 74.9% obtained was with NiMo/zeolite. The results from using the NiMo/zeolite catalyst showed the advantage of having the hydrocracking selectivity from the zeolite and the hydrogenation activity from the NiMo. The different catalysts did not have any differential effect on production of the hexane solubles from the three component coprocessing reactions. All of the catalysts with hydrocracking activity resulted in similar amounts. Only slight differences were observed in the gas production.

Simulated distillation of the hexane soluble fraction from each of these reactions was performed to determine the boiling point distribution of the products produced. The fractions that were determined were gasoline (~180 °C), naphtha (170 to 290 °C), heavy oil (260 to 350 °C), and lubricant (~300 to 370 °C) as shown in Table 4. The reaction of LDPE alone produced the largest amount of material boiling less than 370 °C while the reactions with LDPE and coal produced the lowest weight percent. The type of catalyst employed affected the weight percent of material boiling less than 370 °C for LDPE with the hydrocracking catalysts yielding the highest amounts, but catalyst type had little effect on the products produced from the other two types of reactions.

CONCLUSIONS

The coprocessing of LDPE with coal and petroleum resid was affected by catalyst type. The presence of hydrocracking selectivities during reaction increased conversion and production of hexane soluble materials in the LDPE reaction. Reaction temperature also strongly affected the conversion and the product slate in the LDPE reactions. None of the catalysts affected either the conversion or product distribution from the coal/ LDPE system at the reaction conditions used. Longer reaction time experiments are currently underway to determine if these catalysts influence the two component reaction to any appreciable extent. Simultaneous reactions of LDPE/resid and coal also responded to the different selectivities of the different catalysts. At reaction conditions of 60 min and 430 °C, catalysts with substantial hydrocracking activity yielded higher levels of conversion and hexane soluble material than did the reaction with NiMo/Al₂O₃. Catalysts, like NiMo/zeolite and the 10% Z-753 in NiMo/Al₂O₃, with combined hydrogenation and hydrocracking selectivities, affected the three component system most positively, producing the highest yields of hexane solubles and conversion to THF soluble materials.

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Table 1. Effect of Reaction Temperature and Time on Reactions with Different Catalysts*

Catalyst*	Product Distribution (%)					Conversion (%)	Recovery (%)
	gas*	HXs	TOLs	THFs	IOM		
430 °C, 60 min							
LDPE with Z	24.5±1.3	69.7±1.2	-	-	5.8±2.1	94.2±2.1	55.6±2.3
LDPE with NZ	37.1±1.2	56.0±1.3	-	-	6.9±2.6	93.1±2.6	54.9±2.8
430 °C, 30 min							
LDPE with Z	19.6±1.1	22.6±1.4	-	-	57.8±1.9	42.2±1.9	91.5±1.9
LDPE with NZ	28.5±0.8	23.7±1.6	-	-	47.9±1.8	52.1±1.8	84.6±0.7
400 °C, 60 min							
LDPE with Z	20.2±0.4	5.1±1.4	-	-	74.6±1.1	25.4±1.1	94.2±1.5
LDPE with NZ	22.1±0.7	6.5±0.9	-	-	71.5±2.0	28.5±2.0	92.1±1.7
400 °C, 30 min							
LDPE with Z	19.2±2.1	16.5±0.7	-	-	64.3±0.7	35.7±0.7	89.7±1.1
LDPE with NZ	22.7±1.7	9.4±1.1	-	-	67.9±1.4	32.1±1.4	94.1±2.4

* Reaction conditions : 8.3 MPa H₂, 1g of reactant, 1 wt% catalyst of total feedstock.
 Z = Zeolyst 753 catalyst, NZ = NiMo/zeolite
 gas = gaseous products; HXs = hexane solubles; TOLs = toluene solubles; THFs = THF solubles; IOM = insoluble organic matter which is calculated on an ash-free basis.

Table 2. Factorial Design Analysis for LDPE Reaction with Two Different Catalysts

		A*	B	C	AB	AC	BC
gas	0	84.2	90.0	83.5	103.5	103.0	98.0
	1	109.7	103.9	110.4	90.4	88.9	95.9
	delta*	25.5	13.9	26.9	13.1	16.1	2.1
HX	0	37.5	72.2	113.9	151.6	101.3	101.6
	1	172.0	137.3	95.6	57.9	108.2	107.9
	delta	134.5	65.1	18.3	93.7	6.9	6.3
Conversion	0	121.7	162.1	197.5	255.1	206.3	199.5
	1	281.6	241.2	205.8	148.2	197.0	203.8
	delta	159.9	79.1	8.3	106.9	9.3	4.3

* A=temperature, B= time, and C=catalyst.
 * The higher the delta is, the stronger effect that factor has.

Table 3. Effect of Catalyst Combination on Selected Coprocessing* Systems

Reaction Combination	Catalyst N, Z, or NZ*	Product Distribution (%)					Conversion (%)	Recovery (%)
		gas*	HXs	TOLs	THFs	IOM		
430 °C, 60 min								
LDPE	N	19.1±1.0	50.5±2.2	-	-	30.4±1.6	69.6±1.6	93.9±3.3
	10% Z in N	21.0±0.9	55.3±1.8	-	-	23.7±2.0	76.2±2.0	82.6±2.5
	Z	24.5±1.3	69.7±1.2	-	-	5.8±2.1	94.2±2.1	55.6±2.3
	NZ	37.1±1.2	56.0±1.3	-	-	6.9±2.6	93.1±2.6	54.9±2.8
Coal/LDPE	N	9.8±0.8	25.3±0.6	3.4±0.3	4.3±1.5	57.1±1.3	42.9±1.3	96.3±1.2
	10% Z in N	9.7±1.5	23.7±0.9	4.2±1.1	3.7±1.1	58.7±1.4	41.3±1.4	98.3±2.2
	Z	9.8±1.1	24.5±1.1	4.2±0.7	5.0±0.4	56.5±0.6	43.5±0.6	97.4±1.0
	NZ	10.7±1.9	23.9±0.8	3.5±0.6	4.2±0.5	57.7±2.8	42.3±2.8	97.7±1.1
Coal/Manji/LDPE	N	7.4±1.2	38.3±0.8	8.9±2.1	7.1±1.1	38.3±2.2	61.7±2.2	98.4±0.9
	10% Z in N	7.7±1.7	45.3±0.3	8.3±1.3	7.6±0.3	31.0±0.9	69.0±0.9	96.5±1.1
	Z	8.5±0.8	43.7±0.4	8.7±2.2	7.1±1.1	32.0±1.1	68.0±1.1	97.7±1.2
	NZ	8.4±0.4	45.2±2.1	9.5±1.1	11.8±0.9	25.1±2.3	74.9±2.3	96.5±2.4

* Reaction Conditions : 430 °C, 60min, and 8.3 MPa H₂ introduced at ambient temperature. Reactant loading : 1g of coal (Blind Canyon DECS-17), 1g LDPE, 1.5 g resid (Manji).
 N = Presulfided NiMo/Al₂O₃, Z = Pretreated Z-753, NZ= NiMo/Zeolite. 1 wt% catalyst loading on total charge basis.
 * gas = gaseous products; HXs = hexane solubles; TOLs = toluene solubles; THFs = THF solubles; IOM = insoluble organic matter which is calculated on an ash-free basis.

Table 4. Simulated Distillation of Hexane Solubles from Coprocessing Reactions*

Catalyst*	Weight %						
	SIMREC ^b	Gasoline ^c	Naphtha	Heavy oil	Lubricant	Total with gas	
LDPE	N	73.7	1.7±0.9	6.8±1.3	7.9±1.4	6.8±1.3	42.3±1.4
	10% Z in N	74.3	2.5±1.0	7.1±1.4	8.7±1.6	7.4±1.4	46.7±1.6
	Z	65.3	2.4±1.1	8.7±1.7	13.1±2.0	10.0±1.8	58.7±2.0
	NZ	52.5	2.1±0.8	5.4±1.2	7.6±1.4	5.6±1.2	57.8±1.4
Coal/ LDPE	N	51.4	0.9±0.4	2.1±0.6	3.0±0.7	2.3±0.6	18.1±3.0
	10% Z in N	59.9	0.8±0.4	2.3±0.6	3.5±0.8	2.7±0.7	19.0±3.5
	Z	57.8	0.9±0.4	2.6±0.6	3.4±0.7	2.6±0.6	19.2±0.7
	NZ	64.1	0.7±0.4	3.2±0.7	3.8±0.8	2.9±0.7	21.3±0.8
Coal/ LDPE/ Manji	N	63.8	1.2±0.6	5.1±1.0	5.7±1.1	4.6±1.0	24.0±1.1
	10% Z in N	65.0	1.7±0.8	5.7±1.2	6.5±1.2	5.4±1.1	27.1±1.2
	Z	65.5	1.2±0.7	6.1±1.2	7.0±1.3	5.6±1.1	28.3±1.3
	NZ	70.3	1.4±0.8	6.1±1.2	7.7±1.4	6.2±1.2	29.7±1.4

* 430 °C, 60 min. 8.3 MPa H₂. 1 wt % catalyst loading on the total charge basis. Reactant roading : 1g of coal (Blind Canyon DECS-17), 1g of LDPE, and 1.5g of Manji resid.
^b N = NiMo/Al₂O₃, Z = Z-753, NZ = NiMo/Zeolite.
^c SIMREC = Simulated distillation recovery.
^d Gasoline < 180 °C, 170 °C < Naphtha < 290 °C, 260 °C < Heavy oil < 350 °C, 300 °C < Lubricant < 370 °C.

Figure 1. Product Distribution Trends for LDPE Reaction

