COPROCESSING OF PLASTICS WITH PETROLEUM RESIDUES

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ABSTRACT

The recycling of waste plastics has become an increasingly important issue in recent years due to the enormous use of plastics in almost every aspect of modern life. Considering current conditions and expected future trends of the Saudi economy, the coprocessing of waste plastics with petroleum resid appears to be an attractive option for further studies. Our present ongoing study evaluated the effects of three different catalysts on the conversion and product distribution obtained from the coprocessing of heavy petroleum resid and waste plastics. The plastics used in this study were model polyethylenes (LDPE and HDPE), polypropylene, and polystyrene as well as post consumer waste plastics. The coprocessing of various plastics with petroleum resid was found to be affected by catalyst type. The presence of hydrocracking selectivities during reaction increased conversion and product distribution of hexane soluble materials. At reaction conditions of 60 min and 430°C, catalysts with substantial hydrocracking activity yielded high levels of conversion to liquid fuel products. The coprocessing of waste plastics with resid appears to be a feasible process by which to convert resid and waste plastics simultaneously to liquid fuels and to upgrade both the resid and waste plastics materials.

Keywords: *plastic recycling, coprocessing, coliquefaction, depolymerization, waste management*

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1. INTRODUCTION

Landfill disposal of solid waste is no longer acceptable as a means for dealing with waste in a sustainable manner. Consequently many countries including Kingdom of Saudi Arabia are seeking new ways to conserve our natural resources and reduce waste destined for landfills. Thermal cracking (pyrolysis) is receiving increased attention for the recovery of energy resources from organic solid waste stream. The amount of plastic waste in Saudi Arabia is about 15-wt% in the composition of domestic municipality waste. A number of options are available for handling waste plastics, which include segregation and processing to produce a reusable plastic material, controlled thermal cracking to give mixed hydrocarbons capable of re-polymerization or using the waste purely for energy purposes. Finally, the plastic waste management depends on the relative cost-effectiveness of the above options; some of these options are more cost effective than others. Depolymerization has been shown to be technically feasible, but the cost of this approach makes it undesirable at present. However, current efforts of chemical process recycling have focused chiefly on co processing waste plastics with coal [Andersen et al. 1993, Ding et al.1996, Gollakota et al. 1995 and Taghiei et al. 1993]. The petroleum residue, having a composition that includes both aromatic and aliphatic compounds, appears to be a more compatible material than coal for co processing with waste plastics [Joo et al.1996]. Considering current conditions and expected future trends of the Saudi economy, the co processing of waste plastics with petroleum resid appears to be an attractive option for further studies.

In this study, coprocessing reactions were performed with light Arabian crude oil residues and model plastics. The model plastics that were chosen included low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS). These plastics represent a substantial portion of the waste plastics generated in Saudi Arabia.

2. EXPERIMENTAL

2.1 Materials

The model plastic compounds LDPE, HDPE, PP and PS used in this study were obtained from Saudi Basic Industrial Company (SABIC) and were used as received. The resid used was Light Arabian obtained from Ras Tanura refinery, Saudi ARAMCO. The NiMo/Al$_2$O$_3$ catalyst used in this study was composed of 3.8 wt% NiO and 19.8 wt% MoO$_3$ and was presulfided externally to the reactor prior to use. The catalyst was predried with nitrogen for one hour at 300°C. Then the

catalyst was presulfided by passing a mixture of carbon disulfide/gas oil over the catalyst bed. The final step was to purge with nitrogen for one hour at 100°C, at 320°C for two hours and 350°C for six hours to complete the presulfiding.

The solvents used for extraction analyses were HPLC grade hexane, toluene, and THF form Fischer Scientific.

2.2 Reactions and Procedures

Reactions were performed using single and double components to evaluate the reactivity and interactive effects among the reactants. The following reactions were studied.

Single Component

  (a) LDPE
  (b) HDPE
  (c) PP
  (d) PS
  (e) Resid

Double Components

  (f) Resid/LDPE
  (g) Resid/HDPE
  (h) Resid/PP
  (i) Resid/PS

All reactions were performed in a 25 cm^3 stainless steel tubular micro reactor obtained from Parr. The temperature was kept at 430°C for 60 min at a hydrogen pressure of 8.3 Mpa. Hydrogen was introduced at ambient temperature. The micro reactor was agitated by a built-in mechanical stirrer and heated with a temperature controlled built-in heater.

About 3 to 4 g of resid or polymer were charged to the reactor; resid to polymer ratio for binary reactions was 3:2. All reactions were performed catalytically using 1 wt% presulfided NiMo/Al$_2$O$_3$ powder on a total charge basis. All reactions were at least duplicated.

2.3 Analysis

After the reaction, gaseous reaction products were determined by weighing the tubular microreactor before and after gaseous products were released; this fraction in the product distribution is called gas. The liquid and solid products were analyzed by solvent fractionation, fractionating the products by using a series of solvents. The fractions obtained were hexane-

soluble materials (HXs); toluene-soluble, hexane-insoluble material (TOLs); THF-soluble, toluene-insoluble material (THFs); and THF-insoluble material or insoluble organic matter (IOM), which is calculated on an ash free basis. The masses of the gas, HX, TOL, and THF fractions were determined after the fractioning solvent was removed by rotary evaporation and the fractions were air-dried for 15 h. The weight percentage of each of these fractions was determined and then the percent of the HX fractions was determined by difference. The percentage of HXs is defined as 100 – (gas + TOLs + THFs + IOM). The solubility of the unreacted materials was also obtained using solvent fractionation.

The recovery from these reactions was defined as
$$\% \text{ Recovery} = (\text{g of output}/\text{g of input}) \times 100 \quad (1)$$

Percent conversion was calculated from the following expression (2)

$$\% \text{ Conversion} = \left[1 - \frac{\text{g of IOM}}{\text{g of total charge}} \right] \times 100$$

2.4 Simulated Distillation

The boiling point range of the HX fraction from the different reactions was obtained by simulated distillation using ASTM method D-2887.

2.5 Analysis of Solid Reaction Residues by FTIR

The solid residues (IOMs) obtained from the reactions of LDPE and Resid/LDPE were analyzed using a Perkin Elmer Model 1610 FTIR with IRDM software. Mull samples were prepared by using Fluorolube™ and Nujol™ as mulling agents, following a method described in the literature [Koeing, J. L., 1999]. The samples were prepared by grinding 20 to 30 mg of the solids using an agate mortar and pestle, weighing 12 mg of solid and putting it into a constant volume mulling agent. The mull was spread evenly on a NaCl salt plate and analyzed by FTIR. Each spectrum was performed in the same manner: Spectral scans were obtained with a spectral resolution of 4 cm^{-1} in the 3400 to 700 cm^{-1} spectral domain. Two spectral ranges were analyzed: 2700 to 3100 cm^{-1} using Fluorolube as the mulling agent and 700 to 800 cm^{-1} using Nujol as the mulling agent. The peak heights of the absorbances at 2954, 2915 and 2846 cm^{-1} were measured from a baseline drawn at the base of the absorbances. The presence and relative peak heights of absorbances at 730 and 720 cm^{-1} were also determined and their ratio gave a measure of the crystallinity of LDPE.

3. RESULTS AND DISCUSSION

3.1 Properties of Resids (454°C+) from Saudi Crude Oils

Table 1 shows the properties of 454°C+ (850° F+) residues from the four Saudi crude oils. A comparison of the properties of the residues for the crude oils shows that Arab heavy (AH) and Arab Medium (AM) crude oils have a much higher percentage of materials in the resid fraction than the Arabian Light (AL) and Arabian Extra Light (AEL) crude oils. Similarly AH and AM crude oil residues have greater concentration of carbon residue, sulfur and metals in the residue. The viscosities of AH and AM residues have much higher values in comparison to AL and AEL residues at the same temperature. The pour points of AH and AM crude oil residues are also relatively high.

The residues from the four Arab crude oils were analyzed by proton and carbon-13 NMR spectroscopy. The percentage of aromatic hydrogen (H_{ar}) of AEL and AL crude oil residues were found to be relatively lower, and total aliphatic protons (H_{sat}) relatively higher than AM and AH crude oil residues. The AH and AM residues have a higher aromaticity percentage (C_{ar}) in comparison to AEL and AL.

In view of these properties and also availability of residues from local refineries, the 454°C+ fraction from AL crude oil is selected for this study.

3.2 Solubility Study of Unreacted Raw Material

The experiments were done to establish the solubility of unreacted raw materials (plastics and residues). The solubilities in hexane, toluene and THF are given in Table 2. Initially LDPE, HDPE and PET were primarily insoluble in these solvents, while PS and PVC were soluble in THF. The resid contained about 4% insolubles in n-hexane but more than 99% solubles in toluene and THF.

3.3 Single Component Reactions

Each component used in this study was reacted individually at catalytic reaction conditions. The conversions and product distributions for all the reactions are given in Table 3. The conversion for the simple component reactions show that under similar conditions of temperature and hydrogen pressure both resid and PS undergo nearly complete conversion whereas LDPE and HDPE yielded lower conversions and PP remained in the moderate to high conversion.

3.4 Binary (Plastic/Resid) System

Reactions containing binary combinations of the resid and plastics were studied. The conversion and product distributions for LDPE/Resid system are shown in Tables 4.   The LDPE/Resid yielded a conversion of about 80%. In all the binary system studied, HDPE and LDPE were most difficult plastic to convert in to THF soluble materials.

Gas analysis from different binary systems is shown in Table 5.

The product distribution for the resid/plastic binary systems showed that the largest fraction usually was HX soluble, while toluene and THF fractions were relatively small. Toluene fraction was slightly larger than THF solubles. In all the reactions studied with plastics, LDPE gave the highest yields of gases.

3.5 Analysis of Hexane-Soluble Fractions

The hexane soluble products in the single and binary reactions were analyzed by simulated distillation. The boiling point curves obtained ranged from 70-550°C. The recovery at 550°C was about 80%. The reaction systems that contained LDPE and HDPE had less recovery of material boiling at less than 550°C than systems containing PS or PP.

3.6 Analysis of IOM (insolubles) by FTIR

Each of the reaction systems produced a substantial amount of solids on the completion of the reaction. These solids (IOM) were analyzed by FTIR in order to determine whether these solids were essentially the same for all of the reactions. Also, FTIR was used to evaluate the effect of reaction on the materials used in the reactions.

The differences observed in the FTIR spectra of IOMs obtained from different reaction systems were found to depend on the type of plastics used. These spectra show the characteristic C-H absorbances in the 2800 to 3000 cm^{-1} range for LDPE. The mull samples were prepared in Fluorolube to eliminate any C-H interference by the mulling agent. The measured absorbances were the methyl CH_3 stretching band at 2954 cm^{-1}, CH_2 asymmetric stretching at 2915 cm^{-1}. The addition of resid to LDPE decreased the corresponding peak heights. In this study FTIR is being used to work out the ratios of the methyl and methylene absorbances, (CH_3/CH_2 (as), CH_3/CH_2(s), and CH_2(s)/CH_2 (as). Also the effect of time and temperature of reaction on these ratios will be studied in future.

4. CONCLUSIONS

The coprocessing of waste plastics with petroleum resid is a feasible process by which plastics and resid materials can be converted to liquid fuels. The process is also feasible to upgrade resid. The coprocessing reaction depends on the nature and compatibility of plastics with resid. PS and PP produced a greater proportion of materials boiling at less than 550°C in the hexane soluble fraction than both LDPE and HDPE.

The solid reaction products from different reactions were different to each other and depended mostly on the starting material. Since waste plastics contain additives and fillers that may change the reactivity of systems, therefore further work is required in order to determine the feasibility of coprocessing actual waste plastics with petroleum resides.

ACKNOWLEDGEMENT

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Table 1: Properties of 454°C+ Residues from Arab Crude Oils

Tests	AH	AM	AL	AEL
Residue, °C	454°C+	454°C+	454°C+	454°C+
Residue, °F	850°C+	850°F+	850°F+	850°F+
Specific Gravity @ 15.6°C	1.0150	1.0000	0.9840	0.9600
Gravity, °API	7.80	10.0	12.3	15.90
Viscosity @ 100°C, cst	600	190	104	33
Pour Point, °C	29	24	18	10
Carbon residue, wt% (conradson)	17.5	14.0	11.8	8.5
Sulfur, wt%	4.9	4.7	3.45	2.71
Nitrogen wt%	0.2	0.17	0.14	0.11
Vanadium, ppm	120	48	40	22.4
Nickel, ppm	38	16	14	6.4
Iron, ppm	19	11	9	9.2
H_{sat} %	92.5	91.9	94.0	94.9
H_{ar} %	7.5	8.1	6.0	5.1
C_{ar} %	33.0	35.0	30.1	27.0
Asphaltene wt% (n-pentane insolubles)	12.5	8.5	2.9	0.8

Table 2:. Solubility of the unreacted raw materials

Material	% Weight				Conversion (%)
	Hexane Soluble	Toluene Soluble	THF Soluble	IOM	
LDPE	0.572	4.975	2.089	92.36	7.64
HDPE	0.215	1.121	1.741	96.92	3.08
Polyethylene terphthalate (PET)	0.651	1.121	0.852	97.37	2.63
Polystyrene (PS)	0.571	Soluble 99.9	Soluble 99.9	None	99.9
Polypropylene (PP)	0.785	2.341	1.651	95.22	4.78
PVC	0.05	6.20	Soluble 99.9	None	99.9
Resid	96.07	>99	>99	Nil	99.9

Table 3: Product Distribution from Single Component Catalytic Reacted Materials

Reactant	Product Distribution (%)					Conversion
	Gas	**HX**	**TOL**	**THF**	**IOM**	**(%)**
LDPE	11.6	24.1	3.6	9.5	51.2	48.8
HDPE	9.6	30.7	5.5	4.0	49.6	50.0
PP	2.1	35.6	14.7	19.2	28.4	71.6
PS	5.0	81.5	13.8	0.0	0.0	100
AL RESID	10.3	71.5	10.2	2.5	5.0	94.5

Table 4: Product Distribution from Coprocessing Plastics with Resid

Reactant	Product Distribution (%)					Conversion
	Gas	**HX**	**TOL**	**THF**	**IOM**	**(%)**
LDPE/RESID	3.5	70.7	8.8	1.4	14.6	86.9
HDPE/RESID	5.2	65.5	11.8	2.1	13.1	86.9
PP/RESID	4.2	66.8	8.9	7.8	10.2	89.8
PS/RESID	3.7	87.5	6.0	1.0	1.8	98.0

Table 5: Gas Analysis

Gases\Exp.No.	1	2	3	4	5	6	7	8
H_2	33.9	48.6	90.24	82.53	87.13	93.84	97.87	70.65
N_2	0.92	1.11	1.57	9.63	2.95	1.081	0.881	0.929
CH_4	22.8	19.31	3.67	3.45	3.45	1.563	0.21	5.162
C_2	14.26	11.39	2.11	1.98	2.40	0.975	0.32	6.06
$C_2=$	1.03	0.332	0.04	0.04	0.05	0.053	0.06	0.214
C_3	9.33	7.97	1.24	1.18	1.80	0.667	0.21	6.15
$C_3=$	3.04	1.255	0.14	0.15	0.21	0.153	0.125	1.248
$i\text{-}C_4$	0.71	0.716	0.11	0.10	0.18	0.083	0.005	0.353
$n\text{-}C_4$	4.44	4.04	0.45	0.47	0.785	0.31	0.065	3.567
$t\text{-}2C_4=$	0.51	0.322	0.03	0.03	0.051	0.036	0.011	0.363
$1\text{-}C_4=$	0.965	0.410	0.03	0.03	0.06	0.041	0.026	0.459
$i\text{-}C_4=$	0.311	0.138	0.01	0.01	0.024	0.028	-	0.114
$C_2\text{-}C_4=$	0.34	0.215	0.02	0.02	0.032	0.024	0.008	0.260
$i\text{-}C_5$	0.50	0.552	0.06	0.07	0.14	0.143	-	0.256
$n\text{-}C_5$	1.62	1.59	0.13	0.15	0.288	0.125	0.13	1.540
$1,3\text{-}C_4H_6$	-	-	-	-	-	-	-	-
$3M_1C_4=$	0.03	0.01	-	0.01	-	-	-	-
$t\text{-}2C_5=$	0.22	-	0.01	0.01	-	-	-	-
$2M_2C_4=$	0.07	0.06	0.01	0.01	-	-	-	-
$1C_5=$	0.37	-	0.01	-	-	-	-	-
$2M_1C_4=$	0.10	0.05	-	-	-	-	-	-
$c\text{-}2C_5=$	0.10	0.08	-	0.01	-	-	-	-
Others	1.68	1.51	0.11	0.12	0.465	0.878	0.067	2.678
Total	**97.25**	**99.66**	**99.99**	**100.00**	**100.02**	**100.00**	**99.99**	**100.00**