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Catalytic Conversion of Waste Plastics/Petroleum Resid Mixtures into Transportation Fuels

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Introduction

Waste plastics pose a very serious environmental challenge because of their huge quantity and disposal problem all over the world. Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around six million metric tons per year. The amount of plastic wastes in Saudi Arabia is about 15-wt% in the composition of domestic municipality waste. The land filling of sites and incineration of waste plastics have serious drawbacks. The option of secondary recycling is not showing much significant impact in the recycling industry. Tertiary recycling which return plastics to their constituent monomers or to the higher value hydrocarbon feedstock and liquid fuels is gaining momentum as an alternative method (1). The plastics have been pyrolysed as individual plastics type and mixed plastic waste, however, there are a few studies on the co-processing of plastics with heavy petroleum residues into a variety of fuels (2). The present study is an ongoing research project (KACST AR-18-22) conducted in our laboratory on the catalytic conversion of model and waste plastics with Arabian Light petroleum residue that has provided some important information.

Experimental

Materials. The model plastics that were chosen in this study included low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS). These plastics were used in the coprocessing reactions in the same form as received from the Saudi Basic Industries Corporation (SABIC), Riyadh. The Arabian Light petroleum residue was obtained from Saudi Aramco's Ras Tanura refinery. The solvents used for extraction analyses were HPLC grade hexane, toluene and tetrahydrofuran (THF) from Fischer Scientific.

Catalysts. Selection of a suitable catalyst for cracking reactions is a difficult problem due to limitations in terms of operating conditions, feedstock properties, catalyst performance and desired products. The suitability of solids as heterogeneous catalysts for the cracking processes like in the co-liquefaction of plastic/resid mixtures is based on the four essential characteristics such as activity, selectivity, ease of regeneration and mechanical strength. The NiMo catalyst was used because it has been widely used in coal and resid liquefaction reactions (3,4). The NiO/MoO₃ on Al₂O₃ (NiMo) catalyst was procured from AKZO (KF-843) and composed of 3.8 wt% NiO and 19.8 wt% MoO₃. NiMo was pre-sulfided and dried with nitrogen for one hour at 300°C prior to use.

Methods. 3 g plastics with 0.03 g pre-sulfided NiMo catalyst for single system and 2 g plastics, 3 g resid with 0.05 g catalyst powder for the binary system were charged to the reactor. All reactions were carried out in a 25-cm³ stainless steel tubular micro reactor obtained from Parr at different temperatures, time duration and hydrogen gas pressures. The micro reactor was agitated by a built-in mechanical stirrer and heated with a temperature controlled built-in heater. Reactions were performed using single and double components to evaluate the reactivity and interactive effects among the reactants. The single reactions were studied for: LDPE, HDPE, PS, PP and Resid while the double component reactions were: resid/LDPE, resid/HDPE, resid/PS and resid/PP. All reactions were run in duplicate. A separation procedure for the product distribution of reactions is shown in figure 1.

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

FT-IR Spectroscopy of IOM. The insoluble organic materials (IOMs) obtained from the reactions of model plastics and resid/plastics were analyzed using a Perkin Elmer Model 1610 FTIR with IRDM software. 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. Spectral scans were obtained with a spectral resolution of 4 cm⁻¹ in the region of 3400 to 700 cm⁻¹. The characteristic C-H absorbances 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 characteristic peak heights of C-H absorbance at 2954, 2915 and 2846 cm⁻¹ were measured from a baseline drawn at the base of the absorbance. The presence and relative peak heights of absorbance at 730 and 720 cm⁻¹ were also determined.

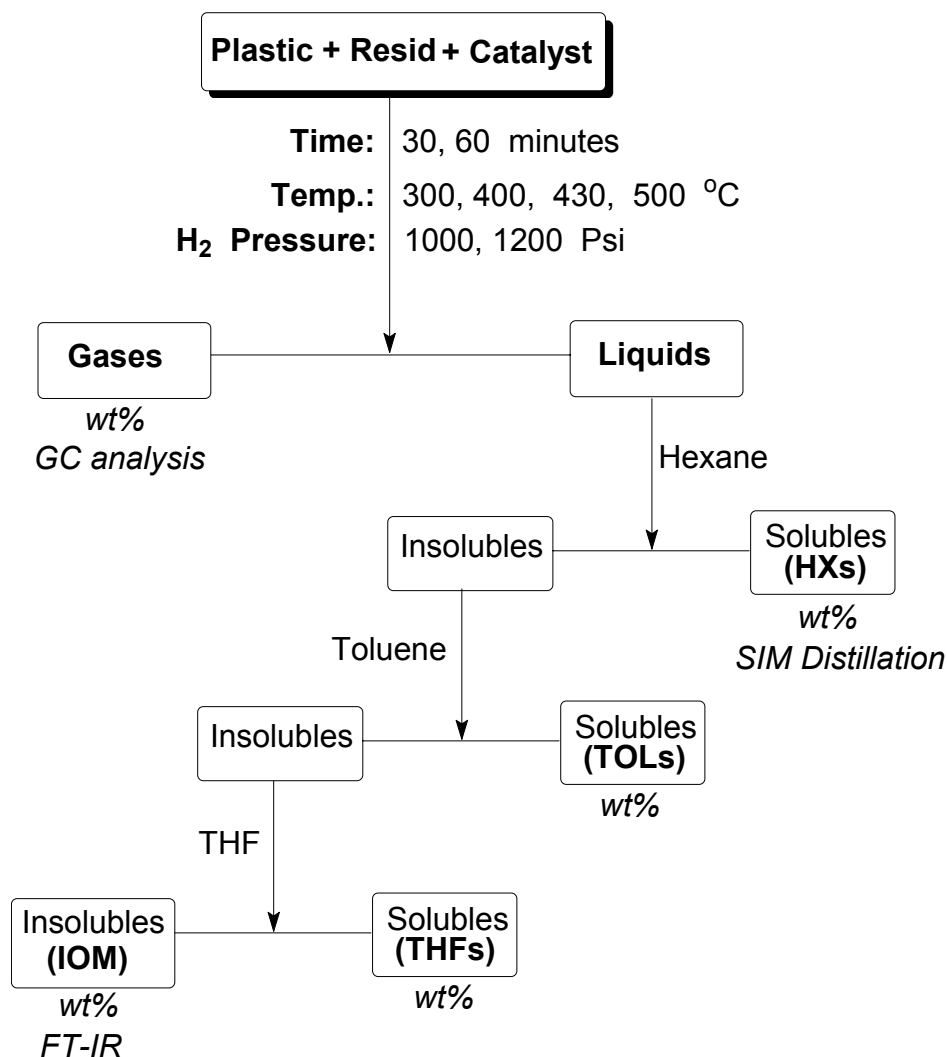


Figure 1. Separation procedure for the product distributions of co-processing reactions.

Results and Discussion

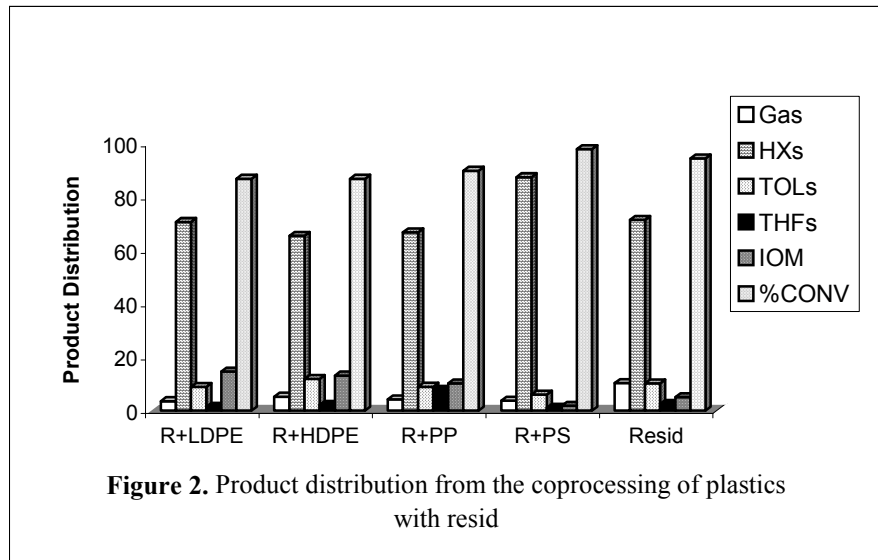
First, the coprocessing reactions of single and binary systems using LDPE and HDPE/resid were experimented at different temperatures (300, 400, 430 and 500 °C), hydrogen gas pressure (500, 1000 and 1200 Psi) and time duration (40, 60 and 90 minutes). The best results, based on the percent conversion and amount of hexane soluble in our study, were obtained at 430 °C, 1200 Psi (8.3 Mpa) and 60 minutes duration.

These optimum conditions were used in our rest of the studies. 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, HXs, TOLs, and THFs 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 HXs fraction was determined by difference. The solubility of the unreacted materials was also obtained using solvent fractionation. Solubility studies of model plastics and resid were performed to establish the solubility of unreacted raw materials in hexane, toluene and tetrahydrofuran (THF) solvents. Initially LDPE, HDPE and PP were primarily insoluble in these solvents, while PS was completely soluble in toluene and THF. The resid contained about 4% insolubles (asphaltenes) in hexane but more than 99% soluble in toluene and THF.

Each component used in this study was reacted individually at catalytic reaction conditions. The conversion for the single 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. The product distributions from single component catalytic reacted materials are given in Table 1. Reactions containing binary combinations of the resid and plastics were studied. The conversion and product distributions from the coprocessing of plastics and resid are shown in figure 2. The LDPE and HDPE/resid yielded a conversion of about 90% while PS was almost completely converted followed by PP. 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. Gas analysis from different binary systems shows that the main gases produced were hydrogen, methane, ethane, ethene, propane, propene, butane and butene.

The typical values of Arabian light crude oil fractionates provided by Saudi Aramco RT refinery are: motor gasoline 32-200 °C with FBP, maximum 225 °C; kerosene and Jet A-1 150-240 °C, FBP, maximum 300 °C and light diesel oil 175-380 °C with no maximum.



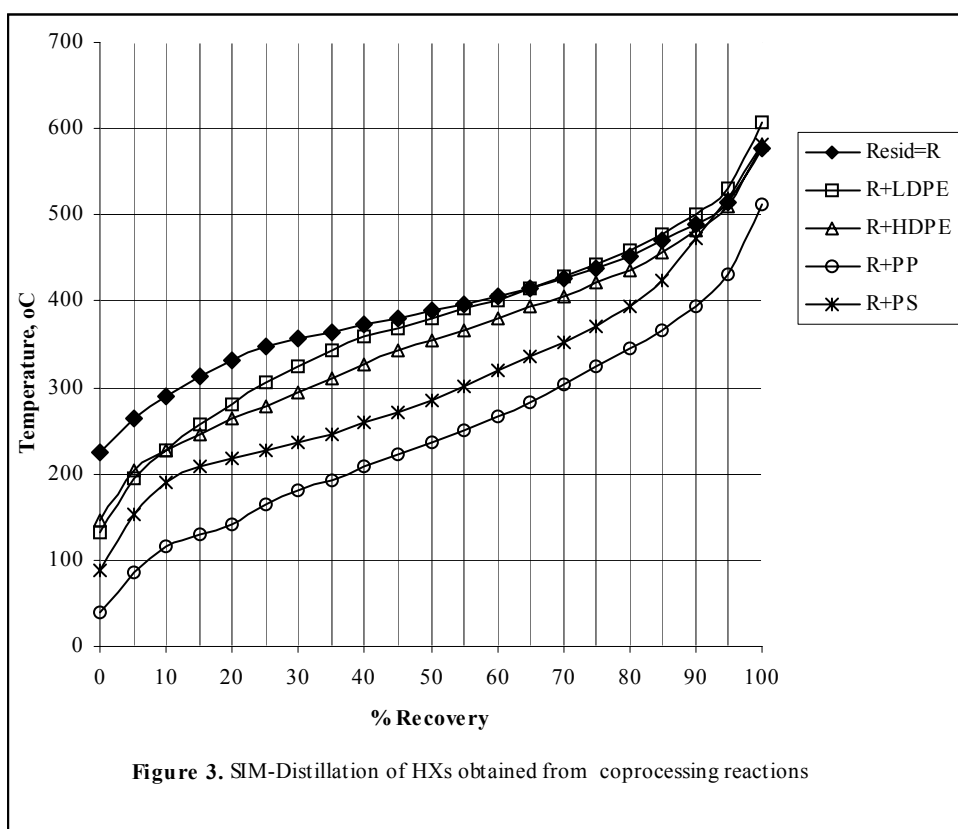
These distillation cut-off points will be used as base line in assessing the extent of conversion of resid/plastics into the transportation fuels. The hexane soluble fractions of the different reaction systems were analyzed using simulated distillation (SIM) and shown in figure 3. The boiling point curves obtained ranged from 70-550°C. The results from the analysis regarding the recovery temperatures of HXs at initial boiling point (IBP) shows 10%, 50%, 90% and final boiling point (FBP). In addition, the amount of gas, gasoline, kerosene and diesel fuels were also found. The SIM results show a general decrease in IBP recovery temperature for the resid/plastic coprocessing reaction as compared to the reaction of resid alone. The recovery at 550°C was about 80%. For PP this decrease is most prominent. The gasoline yield for Resid/PP mixture is also relatively very high. The proportion of material that boiled in the range 300-400 and 400-500°C was found to be relatively larger. Polystyrene produced a much greater amount of material boiling less than 500°C in the hexane solubles. 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. The coprocessing of plastics with resid showed a significant improvement in the conversion rates indicating that the reaction chemistry of resid and plastics are very compatible. These coprocessing reactions appear to depend upon the compatibilities and reactivities of different systems.

Post consumer plastic samples consisting of coke bottles, water bottles, water cups, milk and yogurt bottles were collected. The thermal and catalytic coprocessing of these materials were also studied over NiMo, hydrocracking catalysts. The reaction products were analyzed and given in Table 2. The product distributions

of these plastic types were found to have a very high conversion reaction (79.2-95.8%) affording higher amount of hexane solubles (46-68%).

FT-IR spectroscopy was employed to assess the chemical reactivity of waste plastics with resid. Each of the reaction systems produced a substantial amount of solids (IOM) on the completion of the reaction. These 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 be different depending on the type of plastics used.

In case of model LDPE, the spectra show the characteristic C-H absorbances in the 2800 to 3000 cm^{-1} region. 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 and areas. The absence of prominent peaks and absorbance in the C-H region clearly showed that plastics have been either mostly depolymerized or converted to other liquid products.



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. Reaction temperature and reaction time also strongly affected the conversion and the production of hexane soluble material. The products from the catalytic coprocessing of plastics and resids can be further converted to fuels or chemical feed stocks. 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.

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Table 1: 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
A. Light Resid	10.3	71.5	10.2	2.5	5.0	94.5

Table 2: Summary of Resid/Waste Plastic Conversion and Product Distributions.

REACTANTS	CATALYST	GAS	PRODUCT DISTRIBUTION % WEIGHT						
			HX-S		TOL-S	THF-S	IOM	CONV.	RECV.
			ACTUAL	CAL*					
Resid/coke bottle	NiMo	19.1	45.9	47.9	8.6	9.2	15.2	84.8	98.0
Resid/yogurt bottle	NiMo	12.1	66.5	67.9	11.6	4.3	4.1	95.9	98.6
Resid/white cap of water bottle	NiMo	17.6	67.9	69.3	5.7	3.2	4.2	95.8	98.6
Resid/ water bottle	NiMo	21.9	50.6	51.8	8.1	6.0	12.2	87.8	98.8
Resid/water cup from Arabian Gulf	NiMo	21.78	54.15	55.05	10.10	8.12	4.95	95.05	99.1
Resid/water cup from Al-Watania	NiMo	20.2	57.53	58.23	9.50	7.52	4.55	95.45	99.7

CAL* = CALCULATED