

EFFECT OF POLYOLEFINS ON THERMAL CRACKING OF HEAVY RESIDUES

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INTRODUCTION

Polyolefins, like polyethylene (PE), polypropylene (PP) and polystyrene (PS) represent a major source of plastic waste. Annually in Canada, approximately 50 kilograms of organic waste per person is post consumer plastic and over 40% of this plastic is PE. Less than 5% of the latter is recovered or recycled. However, the PE as well as the PP are the richest polyolefins in hydrogen content; they have the highest H/C ratio, both in term of atomic (1.96) and weight ratio (0.17) of all polymers. This represents a tremendous waste of resources. In an effort to use these resources many different processes are at various stages of development and new innovations continue to be introduced in plastic waste conversion (1-5). Most of them are pyrolytic processes which involve the conversion of polymeric wastes to monomers, chemicals, liquid and gaseous fuels and coke by heating the polymeric material to high temperature without oxygen or in a limited oxygen atmosphere. The decomposition temperatures for PE, PP and PS range from 400°C to 450°C (6). Thermal decomposition of PE and PP is a radical mechanism. Random rupture of C-C bonds in the backbone of the chain yields free radicals (7). PS decomposes thermally by a mechanism which involves a hydrogen transfer at the site of scission. The bond scission is random and yields one saturated and one unsaturated molecule (8).

The objective of this present work was to determine the effect of these radicals produced from polyolefins on the aromatic radicals produced from the heavy residues (vacuum bottoms and bitumen) by analyzing the final effects on thermal cracking products, distillates and coke. A series of experiments has been undertaken using a tubing bomb reactor of 100 mL capacity. The experiments were conducted at 460°C or 470°C for 10 min under an inert atmosphere (N₂).

EXPERIMENTAL

Feedstocks

Cold Lake vacuum bottoms (CLVB) and Athabasca bitumen were used as heavy residues. The polyolefins used as additives were PE, PP and PS, pure resins. The elemental and proximate analyses are given in Table 1. Distillation of the heavy oils to determine pitch content (+525°C) was carried out using an automated D-1160 unit.

Batch reactor unit

The reaction vessel was a 100mL stainless steel tubing bomb reactor. The reactor was charged with 20 g or 30 g of heavy residue mixed with polyolefins at various concentrations. The air from the reactor was purged using high pressure nitrogen. Subsequently, the reactor was depressurized to 1atm at room temperature and then the reactor was immersed in a fluidized sand bed preheated to 500°C. At 460°C or 470°C the reaction was continued for 10 min. The reaction time was defined as the residence time at the desired temperature neglecting the preheating periods that increased with polyolefins concentrations from 6 to 10 min. During reaction, the system is agitated by a pneumatic vibrator which assured good mixing. After 10 min the reaction was stopped by rapidly cooling the reactor by spraying with cold water mists. The gases were vented to a gas sampling bag. The remaining slurry was weighed and distilled or extracted with solvent, toluene or tetrahydrofuran (THF).

Product analysis

Process gases were analyzed by gas chromatography (GC) for H₂, H₂S, CO_x (x=1 or 2) and hydrocarbons up to C₅. The slurry products were distilled using an ASTM D-1160 apparatus to obtain the overall distillable and residue products at a cut point of 525°C (977°F). The overall distillable has been fractionated to determine the amount of naphtha (IBP-185°C), light gas oil (LGO, 185-335°C) and heavy gas oil (HGO: 335-525°C). The residue (+525°C) fraction from D-1160 distillation was extracted by THF for determination of coke which is reported as tetrahydrofuran insolubles (THFI).

The liquid products were analyzed by GC using a capillary gas chromatograph (Perkin-Elmer, Sigma 2000), with a flame ionization detector (FID) and capillary column. Toluene solubles (TS), toluene insolubles (TI), tetrahydrofuran solubles (THFS) and tetrahydrofuran insolubles (THFI) were separated by soxhlet extraction.

RESULTS AND DISCUSSION

The significant feature of this study is the conversion of waste plastics (PE, PP and PS) into transportation fuels, i.e., gasoline or diesel fuel in the presence of heavy residues, through a thermal cracking route. The objectives were to increase the distillate yield, to reduce the amount of residue and to reduce the formation of coke during the thermal cracking process at high temperatures and short residence times. The selected operating conditions must favor the cracking of both feedstocks and additives (polyolefins). Without an external hydrogen source and any hydrogenation catalyst, coke formation would be inevitable at high temperature (460°C or 470°C) even if the reaction time is short (10 min). Any increase in distillate yield or suppression of coke formation can be explained in terms of radical interactions during thermal cracking. The interactions of long aliphatic radicals with aromatic radicals from heavy oils compete with coke formation and other retrogressive reactions. The hydrogen donor ability of polyolefins would convert heavy oil to distillate. The qualities of the distillates produced varied depending on the combination of polyolefins/heavy oils, but this aspect is not addressed in this paper.

Heavy oil feedstocks and polyolefins

Two different feedstocks were used for this study. One is CLVB, which contains a high amount of pitch, 83.2%, high microcarbon residue and high content of sulphur. The H/C atomic ratio is 1.42 and the metals content is low. The second one, Athabasca bitumen, has 52.4% pitch and a lower microcarbon residue. Its H/C atomic ratio is 1.57. The polyolefins were pure, with no additives. The PE (HDPE) has a H/C atomic ratio of 1.96 that is very close to that of its monomer (2.00 for C₂H₄). The PP has H/C ratio of 2.00 and PS a H/C ratio of 1.01.

Effect of polyolefin concentration on product distribution

Distribution of the products obtained by the thermal cracking of Athabasca bitumen in the presence of different polyolefins (PE, PP and PS) at 460°C and 10 min residence time under nitrogen atmosphere is shown in Table 2. A comparison of polyolefins performance based on product yields was made by using polyolefins concentrations, from 0 to 20 wt %. The first four lines of Table 2 show the composition of the reactants in terms of bitumen and polyolefins concentrations. The distillate yields including losses show an increase from 67.3 to 75.5 wt %. Losses are considered as light distillate. The non-distillable material decreased from 27.1 to 18.2 wt % for the run containing 13.5 wt % PE and 6.5 wt % PS. Asphaltenes + preasphaltenes (THFS from distillation residue) yields were almost constant for 20 wt % polyolefins additions. The mixture of PE and PP had a slightly lower effect on residue quality compared with 20% PE. Coke (THFI) yield was constant for the three polyolefins concentrations and 32% lower than the run without polyolefins (Figure 1). The amount of gases increased in the presence of PE+PP and PE+PS compared to PE only. The distribution of products obtained from CLVB in the presence of PE is shown in Table 3. For these runs the distillates were not analyzed, the study concentrated on preasphaltenes (THFS) variation and coke (THFI) suppression (Figure 2). A significant effect on THFS was observed at 5% PE compared to 0% PE. The coke yield decreased with increasing PE concentration. Yields of gases in the presence of PE were almost constant with one discrepancy at 15% PE.

The final pressure at reaction temperature decreased with increasing polyolefins concentration. Table 4 shows final pressures for selected runs in the presence of PE. The gas composition indicates an increase in hydrogen consumption.

Effect of polyolefins concentration on distillates

The composition of distillate products (IBP-525°C) for selected runs are shown in Figure 3. The addition of polyolefins resulted in a significant increase in the naphtha fraction including the loss. However, comparable HGO fractions were obtained for the five runs. Naphtha fraction was the highest (45.3% of the total distillate) in the presence of PS. Minimum increase of 1.7% of distillates was estimated for a 20% addition polyolefins (Table 2).

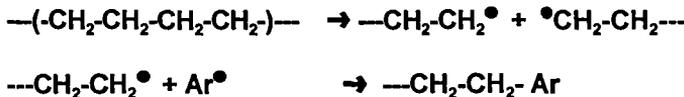
Effect of polyolefins concentration on coke suppression

Figure 4 shows the effect of polyolefins on coke suppression for selected runs using Athabasca bitumen at 460°C. The mixture of bitumen with PE+PP appears to be the

best polyolefins combination for coke suppression with a maximum coke suppression measured at 20 wt % of polyolefins. Using CLVB and PE only the coke suppression effect was more pronounced (Figure 5). At 20% PE the coke suppression was 44.7%. However, an increase of only 10°C in reaction temperature can offset the effect of polyolefins on coke suppression (Figure 6).

Interpretation of effect of polyolefins on products

At the reaction temperature (460°C) the polyolefins are cracked to produce long chain aliphatic radicals. These radicals can interact with aromatic radicals from heavy oils. The aliphatic radicals play the role of scavengers for aromatic fragments and prevent the recombination of large aromatic radicals to form coke, as follows:



Formation of Ar-Ar (coke) was limited by the interaction of aliphatic radicals with Ar[•] to form ---CH₂-CH₂-Ar.

Conclusions

Addition of polyolefins in the thermal cracking of heavy oils increased the hydrogen to carbon ratio of the feedstock and therefore improved the distillate yields. Competitive radical interactions reduced the retrogressive reactions and had a significant effect on coke suppression.

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Table 1 - Characteristics of feedstocks

	CLVB	Athabasca Blumen	PE (HDPE)	PP	PS
D1160 Distillation (wt %)					
S25 9C-	16.6	47.6			
S25 9C+	83.2	52.4			
Microcarbon residue (wt %)	17.1	14.3			
Relative density (g/ml.)	1.038	1.013	0.98	0.89	1.06
Elemental analysis (wt %)					
(as received)					
Carbon	78.6	83.3	85.3	85.3	91.9
Hydrogen	9.3	10.9	13.9	14.2	7.7
Nitrogen	0.6	0.6	-	-	-
Sulphur	5.5	4.6	-	-	-
Oxygen	0.9				
V, Ni, Fe (ppm)					
(as received)					
Vanadium	235	197.0			
Nickel	83	74.0			
Iron	18	700.0			

Table 2 - Distribution of products obtained from bitumen
in the presence of PE, PP and PS

Feed wt %					
Athabasca bitumen	100.0	80.0	80.0	80.0	73.0
PE	0.0	20.0	13.5	13.5	20.0
PP	0.0	0.0	6.5	0.0	7.0
PS	0.0	0.0	0.0	6.5	0.0
	Yields wt %				
Distillate	64.3	69.1	62.7	65.8	69.4
THFS	18.1	11.3	12.6	10.5	14.2
THFI	11.0	7.5	7.7	7.7	4.7
Residue:THFS+THFI	27.1	18.8	20.3	18.2	18.9
Gases	5.6	5.8	6.6	7.3	5.5
Total	97.0	93.7	89.6	91.3	83.8
Loss	3.0	6.3	10.4	8.7	6.4
Extra distillate produced by feedstock mixture*	—	4.0	1.7	3.1	1.9

* - Based on distillate from bitumen only: eg. [(69.1+6.3)-(64.3+0.6+20)]

Table 3 - Distribution of products obtained from CLVB in the presence of PE

CLVB wt %	100.0	95.0	90.0	85.0	80.0	70.0	50.0	0.0
PE wt %	0.0	5.0	10.0	15.0	20.0	30.0	50.0	100.0
	Yields wt %							
TS	76.3	78.7	80.3	87.3	87.9	87.9	91.4	97.7
THFS	1.7	4.9	2.3	2.1	0.6	1.4	0.2	0.2
THFI	18.3	14.8	14.0	8.7	8.2	7.3	5.9	1.0
Gases	3.7	3.8	3.4	1.9	3.3	3.4	2.5	1.1

Table 4 - Final pressure at reaction temperature of PE with heavy oils
and hydrogen concentration in gases
Initial pressure: 1atm at room temperature (nitrogen)

PE, wt %	0.0	10.0	15.0	20.0	50.0	100.0
Feed:						
CLVB						
wt %	100.0	90.0	85.0	80.0	50.0	0.0
	Final Pressure					
psi	980.0	950.0	925.0	1080.0	900.0	620.0
Atm	66.8	64.8	63.1	73.6	61.3	42.3
H ₂ wt %*	9.2	9.1	9.2	9.2	6.7	18.3
H ₂ ** consump.	—	1.0	2.3	1.8	7.1	—
Feed:						
Bitumen,						
wt %	100.0	90.0	85.0	80.0	50.0	0.0
	Final Pressure					
psi	1468.0	1417.0	1100.0	887.0	874.0	620.0
MPa	100.1	96.6	75.0	59.1	45.9	42.3
H ₂ wt %*	6.5	6.4	6.4	9.1	12.1	18.3
H ₂ ** consump.	—	1.3	1.9	-0.3	0.3	—

* - Hydrogen concentration in gases

** - Based on 100% polyolefins

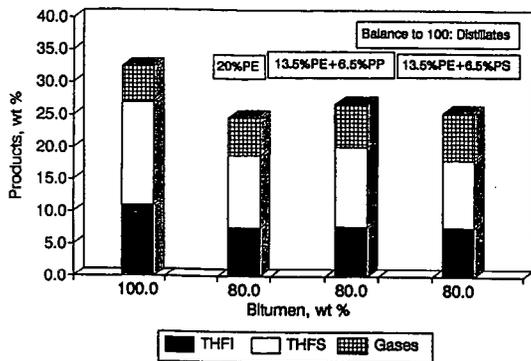


Figure 1. Effect of polyolefin types on products formation from bitumen

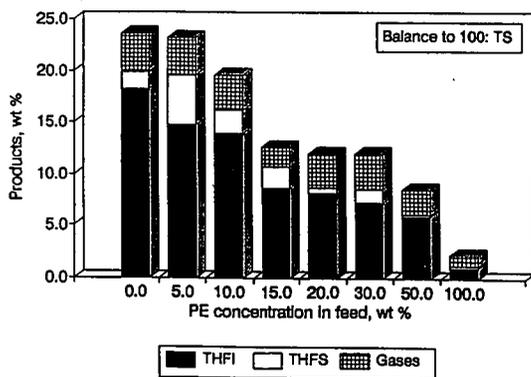


Figure 2. Effect of PE concentration on products formation from CLVB

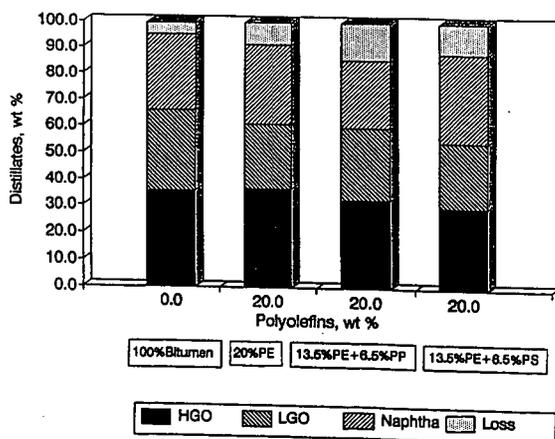


Figure 3 -Effect of polyolefin types on distillates composition from bitumen

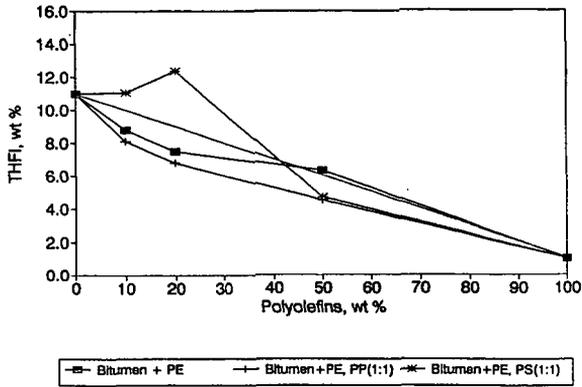


Figure 4 -Effect of polyolefins concentration on coke formation

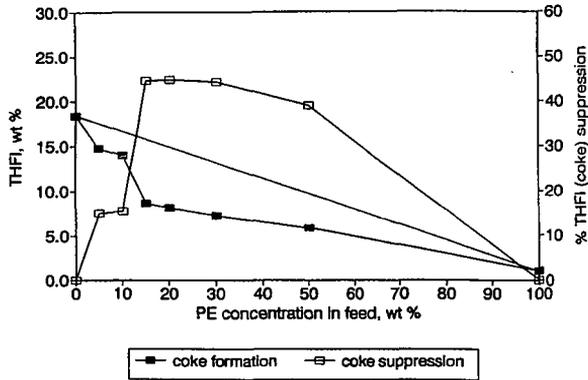


Figure 5 -Effect of PE concentration on suppression of coke from CLVB

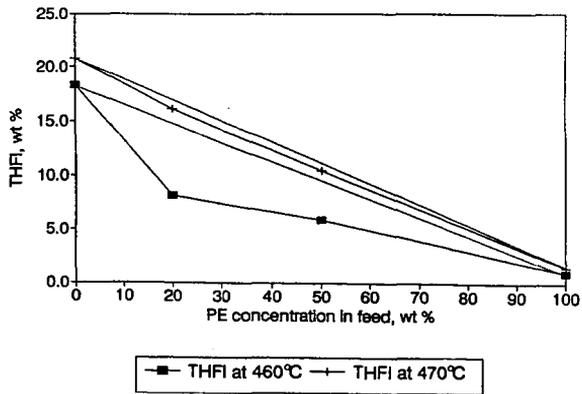


Figure 6 -Effect of temperature on suppression of coke from CLVB