

EVALUATION OF TWO STAGE PROCESSING OF WASTE PLASTICS WITH COAL AND PETROLEUM RESID

Hyun Ku Joo, Christine W. Curtis^a, and James M. Hool^b

^aChemical Engineering Department

^bIndustrial Engineering Department

Auburn University

Auburn, Alabama 36849

KEYWORDS: coprocessing coal, resid, waste plastics, post consumer plastics, fractional factorial design

ABSTRACT

Two stage coprocessing of waste plastics with coal and petroleum resid was investigated using a one-third factorial design. In the two stage process, waste plastics were reacted in the first stage and the liquid products from the first stage were introduced into the second stage which consisted of coal and petroleum resid. Four factors were evaluated in the study including the type of catalyst, the weight percent of coal, and the compositions of plastic and resid. The catalysts investigated included NiMo/Al₂O₃, NiMo/zeolite, and HZSM-5; the weight percents of coal investigated were 0, 10, and 29%; the plastics investigated were low density polyethylene (LDPE), polystyrene, and mixed plastics; and the resids used were Manji, Maya, and Hondo. The results from these factorial experiments were evaluated by determining their distributions using solvent fractionation. The production of gas and hexane soluble materials as well as the conversion to THF soluble materials was determined. The significance of each factor for producing these products and converting the two stage materials was determined and compared.

INTRODUCTION

The direct coprocessing of waste plastics with coal in a single stage reaction presents problems in effectively converting each material for the reaction conditions, and the catalyst needed for each material are quite different. (Luo and Curtis, 1996 a, b) Two stage coprocessing in which the waste plastics were reacted and the resulting product then used as a solvent for coal, allowed for customizing the reaction conditions and catalysts for the needs of each material. (Luo and Curtis, 1996 c; Luo, 1997; Ding et al., 1996) Previous research has shown that incorporating a solvent such as petroleum resid, which has been used previously as a solvent for the coprocessing of coal (Speight and Moschopedis, 1986; Yan and Espencheid, 1983; Curtis and Hwang, 1992; Curtis et al., 1987a,b; Guin et al., 1986), into the reaction effectively provides a bridging solvent in which the two chemically incompatible coal and waste plastics can be coprocessed effectively. (Joo and Curtis, 1996a; 1996b; 1996c; 1997a)

Two stage coprocessing of coal, waste plastics, and resid has been explored to determine the most effective method of staging the reactions and the best sequencing of reaction conditions. (Joo and Curtis, 1997 b) The results indicated that converting the waste plastics in the first stage under fairly severe conditions, and then reacting the first stage product in the second stage with coal and resid under less severe conditions, converted the most material to liquid products. The previous study involved LDPE only as the waste plastic material. The current study extends that research and involves post consumer plastics obtained by crushing and grinding commercially available plastic products and by using post consumer plastics collected in Germany. This study uses a one-third fractional factorial design to determine the effect of four factors, the types of catalyst, waste plastic, and resid used, and the coal concentration, on the products from two stage coprocessing of waste plastics, coal and resid. Each of these four factors was tested at three levels. The efficacy of the two stage coprocessing was evaluated by quantitatively determining the relation between the chosen factors and response variables which were the product fractions produced.

EXPERIMENTAL

Materials. A mixture of waste plastics including polystyrene (PS), polypropylene (PP) and low density polyethylene (LDPE) was made by chopping and subsequently grinding trash baskets and disposable plates. Post consumer LDPE was also used as an individual reactant. A waste

plastics mixture obtained from a German recycling company was supplied to us by Dr. Gerald P. Huffman of the University of Kentucky. In addition, post consumer LDPE was also used. Blind Canyon DECS-17 bituminous coal, obtained from the Penn State Coal Sample Bank, was used in this study. 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 resids used in the coprocessing reactions were Manji, Maya, and Hondo which were obtained from Amoco. These resids had different amounts of their material boiling in the range of 650 to 1000 °F: Manji had 1.24%, Hondo, 6.58%; and Maya, 19.0%. The remaining material boiled above 1000 °F. The catalysts tested in the study were NiMo/Al₂O₃ (Shell 2.72 wt % Ni and 13.16 wt % Mo), NiMo/zeolite (Akzo, <25 wt % MoO₃ and 1-10 wt% Ni₂O₃ with ultrastable zeolite), and HZSM-5 (United Catalysts). The NiMo/Al₂O₃ catalyst was presulfided and powdered prior to use. The catalysts were introduced into each stage at a level of 1 wt% on a total charge basis.

Reaction Procedures. This study involved a factorial design in which the effect, composition, and concentration of the reactants and type of catalyst were evaluated. The design parameters and their levels are presented in Table 1. Two stage reactions were performed in which the plastic was reacted in the first stage. The total first stage product without extraction was added to the second stage coprocessing reaction. The second stage reaction contained resid and either 0, 10, or 29 wt % coal. The reactions conditions in the first stage were 430 °C, 60 min and 500 psi (3.4 MPa) of H₂, introduced at ambient temperature. The second stage reaction conditions were 430 °C, 30 min and 1200 psi (8.3 MPa) of H₂, introduced at ambient temperature.

Analysis. The solid and liquid reaction products were analyzed by solvent fractionation using a series of extraction solvents. The amount of gaseous products was determined by weighing the gaseous products before and after they were released from the reactor. The liquid products were fractionated by using a series of solvents, into hexane soluble (HXs), toluene soluble, hexane insoluble (TOLs), THF soluble, and toluene insoluble (THFs) materials, or IOM, defined as insoluble organic matter that is moisture and ash-free. Conversion was defined as:

$$\%Conversion = [1 - \frac{gIOM_{ndf}}{gTotalCharged_{ndf}}] \times 100$$

EXPERIMENTAL DESIGN

Catalytic two stage coprocessing of post consumer plastics, resid, and coal was performed to evaluate the effect of different sources and compositions of plastics and resids on the final products obtained. In addition, the effect of having coal present at different concentrations in the coprocessing reaction was also an important aspect of this research. The four factors that were selected for analysis in this study were catalyst type, post consumer plastic type, resid type, and coal content. Three levels for each factor were chosen for the purpose of investigating the effect of different types of catalysts, plastics and resids as shown in Table 1. The effect of having coal present as nearly one-third of the reactants in the second stage reaction, as only a small (10%) portion of the total second stage reactants, or not at all, was evaluated in terms of product distributions and conversion.

The total number of factor-level combinations (FLCs) used was 3⁴ = 81. A one-third (1/3) fractional factorial design was used for this study, therefore, 3⁴⁻¹ = 27 FLCs were required. The effects that were selected to be sacrificed were I = AB²CD = (AB²CD)², each of which had two degrees of freedom (df). The effects that were investigated in this design were: (1) the main effects (8 df) A, B, C, D, each with 2 df; and (2) the two factor interactions AB, BC, A × C = AC, AC², A × D = AD, AD², C × D = CD, CD², with a total of 18 df.

RESULTS AND DISCUSSION

The one-third fractional factorial design required that 27 two stage coprocessing reactions be performed. The factor levels that were chosen and the reactions that were performed are given in Table 2. The first column describes the type of post consumer plastic used in the first stage, the

type of resid used in the second stage, and the type of catalyst used in both stages. The second column describes the coal weight percentage, ranging from 0 to 29 wt %, that was used in the second stage. The next four columns describe the product distributions achieved in the reaction. The last two columns are the conversion to THF soluble products and the recovery, respectively.

The first stage of the two stage sequence was performed using one of the three types of plastics, with a sufficient amount of plastic (usually about 5 g) being introduced so that 2 g of the first stage reaction product was produced for use as a solvent in the second stage. The reactants in the second stage reaction were the first stage reaction product, the resid chosen from the factorial design, and coal, if present in the reaction. The conversion that is described is the conversion of the reactants entering the second stage to THF soluble products. The recovery was also based on the second stage only, therefore, the first stage conversion and recovery were not used in these calculations. The loss of converted material in terms of gases and volatiles from the first stage was not considered.

The effect of the different reaction parameters is evident in the product distributions obtained. The amount of gas produced was fairly stable for all of the combinations, and ranged from 8.5 to 13.6%. Much larger ranges were observed in the HXs soluble fraction where the lowest amount of HXs produced was 40.7% and the highest amount was 75.4%. The amount of HXs produced was directly influenced by the amount of coal that was present in the reaction. When coal was present at 29 wt % in the second stage, the HXs ranged from 40.7 to 57.9%; when coal was present at 10 wt %, the HXs ranged from 50.6 to 71.9%; and when no coal was present, the HXs ranged from 50.0 to 75.3%. The highest production of HXs was obtained when no coal or 10 wt % coal was present in the second stage reaction. The range of THF solubles and IOM yielded a greater variability than that observed in the gases, but less than that observed in the HXs.

The conversion also was directly influenced by the type and amount of the reactants, and ranged from 64.6 to 99.0%. The conversions from the second stage reactions ranged from 64.6 to 88.0% when coal was present at 29 wt % in the second stage, and from 72.5 to 93.8% when coal was present at 10 wt % in the second stage reaction. When coal was not present, the conversions ranged from 70.7 to 99.0%. No coal or a low weight percentage (10%) of coal present in the second stage coprocessing reaction yielded higher conversions than those obtained when 29 wt % coal was present. Therefore, not only the presence of the coal but also the other factors, including the type of catalyst, type of waste plastic and type of resid, influenced the conversion of solid reactants.

Analysis of variance (ANOVA) calculations were performed on three product parameters: gas production, HXs production, and conversion. Only the catalyst type affected the gas production at the 0.01 significance level. However, HXs production was much more affected by all of the factors. The type of catalyst, resid, and waste plastic used as well as the weight percent coal all affected the production of HXs materials at the 0.01 significance level. Similarly, the factors of catalyst type, waste plastics composition, and weight percent coal affected conversion at the 0.01 significance level while the resid type affected conversion at the 0.025 significance level. All three parameters, gas production, HXs production, and conversions were affected by the interaction between catalyst type and waste plastics type at the 0.01 significance level. The activity and selectivity of the catalyst used in the first stage reaction strongly affected the products and conversions achieved from two stage coprocessing of coal, waste plastics, and resid.

SUMMARY

The results from the one-third fractional factorial design coprocessing experiment clearly demonstrated that the products from two stage coprocessing reactions were strongly affected by the type of catalyst, waste plastic and resid used, and by the amount of coal present in the second stage reaction. Each of these factors affected the production of hexane solubles at the 0.01 significance level. All of the factors except for resid type affected the conversion at the same level. A strong interaction between the types of catalyst and waste plastic was observed, and affected gas production, hexane solubles production and conversion.

Several consistent trends were observed in the reactions performed. The absence of coal or the presence of coal at low concentrations (10%) resulted in a higher production of hexane solubles and higher conversion. Coal is a difficult material to convert to lighter liquids and requires extensive hydrotreating to produce light products. The two stage coprocessing reaction performed did not

have sufficient selectivity for hydrotreating to produce light products from coal. The conversion was similarly affected by the coal concentration, since again substantial hydrotreating was required to convert coal to THF soluble products. The conversion was also affected by the reactivity of the waste plastic material and by the propensity of waste plastics to be converted to liquid and gaseous products in the first stage. This factorial design demonstrated that through the selection of certain sets of factor combinations that two stage catalytic coprocessing of coal, waste plastics, and resid is a feasible processing method for utilizing waste plastics.

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ACKNOWLEDGEMENTS

The support of the Department of Energy through Contract No. DE-FC22-93PC 93053 is gratefully acknowledged.

Table 1. Factors and Factor Levels

Factors	Levels
Catalysts (A)	NiMo/Al ₂ O ₃
	NiMo/zeolite
	HZSM-5
Resids (B)	Manji
	Maya
	Hondo
Plastics (C)	post-LDPE
	post-Mixture
	European mixture
Weight percent of Coal (D)	0 %
	10 %
	29 %

Table 2. Product Distributions from Post-Consumer Plastics Coprocessing Reactions

Plastic, Resid, Catalyst	Coal weight %	Product Distribution (%)				Conversion (%)	Recovery (%)
		gas	HXs	THFs	IOM		
R, J, NZ	10	9.4	71.9	11.7	7.0	93.0	87.8
D, J, NZ	29	9.5	40.7	14.4	35.4	64.6	99.1
E, J, NZ	0	11.4	71.1	7.4	10.1	89.9	86.1
R, J, NA	29	9.1	57.9	19.7	13.3	86.7	90.4
E, J, NA	10	9.5	60.5	11.6	18.5	81.5	94.1
D, J, NA	0	8.6	63.9	7.0	20.5	79.5	91.0
D, J, Z	10	12.5	69.4	11.3	6.8	93.2	73.7
R, J, Z	0	11.9	75.3	11.8	1.0	99.0	75.1
E, J, Z	29	10.1	46.3	14.4	29.2	70.8	96.4
D, Y, NA	10	7.9	50.6	14.0	27.5	72.5	96.2
R, Y, NA	0	10.3	68.3	16.5	4.9	95.1	82.5
E, Y, NA	29	9.6	42.9	17.2	30.3	69.7	90.5
D, Y, NZ	0	9.3	50.0	11.4	29.3	70.7	95.3
R, Y, NZ	29	10.3	50.0	21.1	18.6	81.4	91.6
E, Y, NZ	10	10.0	56.1	14.5	19.4	80.6	92.2
R, Y, Z	10	11.0	65.0	17.9	6.2	93.8	79.5
E, Y, Z	0	10.0	57.4	14.5	18.1	81.9	90.6
D, Y, Z	29	11.1	45.2	16.7	27.0	73.0	92.9
R, O, NA	10	9.5	61.8	16.4	12.3	87.7	90.0
E, O, NA	0	10.2	62.5	10.9	16.4	83.6	90.5
D, O, NA	29	8.5	42.6	13.5	35.4	64.6	91.1
D, O, NZ	10	10.8	48.9	15.1	25.2	74.8	93.4
R, O, NZ	0	9.1	71.6	11.7	7.6	92.4	82.6
E, O, NZ	29	10.4	48.0	20.2	21.4	78.6	93.1
D, O, Z	0	13.6	73.5	9.7	3.1	96.9	62.2
R, O, Z	29	12.1	54.6	21.3	12.0	88.0	82.9
E, O, Z	10	11.0	61.9	13.1	14.0	86.0	86.3

^a: Fractional factorial design of $3 \times 3 \times 3 \times 3 = 81$ factor-level combinations into three fractions.

^b: 430 °C, 60 min → 430 °C, 30 min, Plastic → Coal + Resid, 500 psi → 1200 psi H₂ introduced at ambient temperature. Reactant: C = Blind Canyon DECS-17. D = Post-consumed LDPE, E = European, R = Mixture of post-consumed LDPE, PP, PS. J = Manji, Y = Maya, O = Hondo. NA = presulfided NiMo/Al₂O₃, NZ = NiMo/zeolite, Z = HZSM-5.

^d: gas = gaseous product, HXs = hexane solubles; TOLs = toluene soluble, hexane insolubles, THFs = THF solubles, toluene insolubles and IOM = insoluble organic matter.