

CATALYTIC TWO STAGE COPROCESSING OF WASTE PLASTICS AND COAL

Mingsheng Luo and Christine W. Curtis
Chemical Engineering Department
Auburn University, AI 36849-5127

Keywords: two stage, coprocessing, waste plastics, coal

INTRODUCTION

The disposal of post-consumer plastics has become an increasingly serious environmental problem throughout the world as well as in the United States. Because of its ever increasing volume, disposal of waste plastics by landfilling is an undesirable option, particularly in densely populated areas. Recycling of plastics is a direct way of reusing the hydrocarbon content in the plastics. (Leaversuch, 1991). However, primary recycling of plastics into the monomer is only accomplished in approximately 2% of the cases (Smith, 1995) and requires that the recycled plastic be separated from the mixed waste. Recycling the mixed plastics wastes to liquid or gases provides a means for reutilizing the hydrocarbons as fuels or chemical feedstock and abstracting the energy or chemical value from the waste material. Pyrolysis and liquefaction of waste plastics as well as liquefaction of waste plastics with coal have been explored by a number of researchers. (Taghiei et al., 1994; Anderson and Tuntawiroon, 1993; Ng, 1995a; Ng, 1995b; Palmer et al., 1995; Huffman et al., 1995)

The supply of waste plastics is limited; even if all of the waste plastics were recycled to transportation fuels, only one month's supply would be available on an annual basis (DOE, 1995). The feasibility of tertiary waste plastics recycling is limited by the availability of waste plastics and the constancy of the supply. Hence, waste plastics liquefaction can provide a valuable addition to our energy supply but will not substantially affect self-sufficiency. Utilization of a native natural resource such as coal in conjunction with waste plastics will not only provide sufficient hydrocarbon resources and a constant feedstock supply but will also provide more self-sufficiency in our energy supply.

In a previous research study, waste plastics were coprocessed directly with coal using commercial hydrotreating catalysts, slurry phase catalysts, zeolite catalysts, and fluid catalytic cracking (FCC) catalysts (Luo and Curtis, 1996 a and b). Since the reactants are composed of chemically different materials, coal being aromatic and most common plastics in the waste stream being polyolefins and aliphatic, these two materials are basically chemically incompatible. The efficacy of the conversion of coprocessed coal and waste plastics to THF soluble material depended upon the plastics composition, efficacy of the catalyst used for the reactant composition, and use of a solvent as well as type of solvent. Coliquefaction reactions of mixtures of waste plastics as well as coprocessing reactions of those mixtures with coal evinced that reaction parameters must be tailored to the waste plastics stream to achieve maximal plastics conversion to liquids. Those reaction parameters were often in conflict with the most efficacious reaction conditions for coal. Typical coal liquefaction catalysts were not sufficiently active to hydrocrack the polyolefins while hydrocracking catalysts were easily and rapidly deactivated in the presence of liquefying coal because of the heavy hydrocarbons and heteroatoms present. Hence, simultaneously coprocessing coal and waste plastics when they are initially both solid reactants does not usually produce an optimal product from either material.

To circumvent the problems associated with simultaneously reacting materials that are inherently so different, two stage processing was investigated. The two stage process was composed of a first stage in which the waste plastics mixture was liquefied and of a second stage where coal was liquefied with the hexane soluble product from the first stage. The reaction conditions and catalysts for each stage were optimized to yield the highest conversion of the reactants to THF soluble and hexane soluble materials in each stage.

EXPERIMENTAL

Materials. The model plastics used in this research were high density polyethylene (HDPE), polyethylene terephthalate (PET), and polystyrene (PS), all of which were obtained from Aldrich. A mixture consisting of 50% HDPE, 30% PET, and 20% PS was used as a base plastics mixture in single and two stage reactions. The solvents used in this study were tetralin and hexadecane, obtained from Aldrich and Fisher Scientific, respectively. The plastics and the solvents were used as received. Illinois No. 6 coal, obtained from the Argonne Premium Coal Sample Bank, was used as received. The catalysts used in this study were fluid catalytic cracking catalysts, Low Alumina and Super Nova-D, which were supplied by Davison Chemical Division of W. R. Grace and Company. A zeolite HZSM-5, obtained from United Catalysts, was also used. The catalysts used for the second stage coal reactions included the slurry phase hydrogenation catalyst precursors, molybdenum naphthenate (6% Mo; MoNaph) and iron naphthenate (6% Fe; FeNaph), obtained from Shepherd Chemical. Both of the slurry phase catalysts were reacted in the presence of excess elemental sulfur, which was obtained from Aldrich.

First Stage Reaction. In the first stage reaction, a waste plastics mixture was liquefied in order to obtain a liquid solvent to be used as the solvent in the second stage coprocessing reaction. The plastics mixture was liquefied in ~50 cm² stainless steel microtubular reactors at 713 K (440 °C)

for 60 min under an initial H_2 pressure of 2.8 MPa introduced at ambient temperature. The reactors were agitated vertically at 450 rpm. Ten grams of plastics mixture were charged to the reactor. The loading for the catalytic reactions using FCC and HZSM-5 catalysts was 10 wt % on a plastics charge basis. Both HZSM-5 and the FCC catalysts were pretreated prior to being used in the reaction by heating the catalysts for 2 hr at 477 K (400 °F) followed by 2 additional hours at 811 K (1000 °F). After the reaction was completed, the reactor was quenched in ambient water. The amount of gaseous products was weighed and the gaseous products were removed. The liquid products were extracted with hexane and the soluble amount determined. The hexane solvent was evaporated from the liquid product which was then used as a coal liquefaction solvent in the second stage reaction.

Second Stage Reaction. The second stage coprocessing reaction was performed with 2 g of coal and 2 g of first stage solvent in 20 cm² stainless steel microtubular reactors at 713 K (440 °C) for 30 min. The reactors were charged with 5.6 MPa of H_2 introduced at ambient temperature and were agitated at 435 rpm during the reaction. Slurry phase MoNaph and FeNaph catalysts at 1000 ppm of active metal and elemental sulfur at 6000 ppm were charged on a total reactant basis. In some reactions, a loading of 500 ppm of MoNaph and 500 ppm of FeNaph was used.

Product Analysis. The liquid products for the second stage reaction were analyzed by solvent fractionation using hexane as the initial solvent followed by THF. Any solid residue left in the reactor after extraction was carefully scraped from the reactor walls. The amount of hexane and THF soluble materials was determined as well as the amount of THF insoluble material or IOM (insoluble organic matter which is ash free). The hexane soluble fraction produced in the first stage was used as the solvent in the second stage reaction.

The recoveries obtained in the reactions were calculated by

$$\text{Recovery} = (\text{g Recovered} / \text{g Charged}) \times 100\%$$

as are given in the tables. The conversion of the solid reactants to THF soluble material was determined on a solvent, moisture, and ash free basis using the equation

$$\text{Solid Conversion} = 100\% - \text{IOM}\%$$

where IOM is produced from reactions of either coal or plastics or both.

RESULTS AND DISCUSSION

Two stage coprocessing of coal and waste plastics was investigated to determine if higher conversion to THF soluble material and higher production of hexane soluble material could be obtained than with single stage coprocessing. Two sets of experiments were performed. The first set of reactions consisted a first stage catalytic reaction using the base plastic mixture. Then coal was placed in the reactor and reacted with the liquefied plastics as well as the unconverted material. The second set of reactions consisted also of two stage processing, but in these reactions the hexane soluble material produced in the first reaction of the base plastics mixture was used as the solvent for second stage coal reaction. The reaction products from each stage were analyzed using solvent fractionation and a determination of the conversion of the solids to THF soluble products:

Two Stage Coprocessing. The first set of the two stage reactions is presented in Table 1. The first stage reaction involved the base plastics mixture consisting of 50% HDPE, 30% PET, and 20% PS that was reacted at 440 °C and 30 min using Low Alumina and HZSM-5 catalysts. Both catalysts promoted plastics conversion to THF solubles of more than 85% and hexane soluble yields 69.8% and 61.5%, respectively. The second stage reaction was performed with coal at 400 °C for 30 min and 5.5 MPa of initial H_2 pressure. The coal was placed in the reactor with the entire reacted base plastics mixture as well as the first stage catalyst. The products obtained from the second stage reaction were similar regardless of the first stage reaction. These second stage reactions produced high levels of gas make of 32.5 and 29.7%, respectively, for the first stage Low Alumina and HZSM-5 catalysts. The conversions from the second stage reactor were similar and low, 57.5 and 54.9%, respectively, for Low Alumina and HZSM-5 first stage catalysts. The second stage hexane solubles were also similar and low, yielding 22.8 and 23.5%, respectively.

Two Stage Coprocessing using First Stage Hexane Solubles as Solvent. The disadvantage of the first set of two stage reactions was the presence of unconverted and difficult to convert plastics in the second stage reaction. In addition, the catalyst from the first stage was present during the coal reaction. These hydrocracking catalysts promoted high gas production during the second stage. Consequently, the reaction sequence was changed to eliminate the presence of both the unconverted material and the hydrocracking catalyst in the second stage. In both stages the reaction conditions were tailored so as to promote the desired reactions during that stage and to minimize the undesirable reactions.

The first stage reaction was performed at 440 °C and 60 min with each of the three hydrocracking catalysts, Low Alumina, HZSM-5, and Super Nova-D, and the base plastics mixture. High conversions to THF soluble materials were obtained with all three reactions yielding 88.4, 94.5, and 95.1, respectively, as shown in Table 2. The majority of the product produced was hexane

soluble material that was extracted for use as the solvent in the second stage. Although gas yields ranged from 14.9 to 17.9%, these products did not affect the second stage reaction and could presumably be used as a fuel.

The second stage reaction employed coal at reaction conditions of 400 °C and 30 min with 5.6 MPa H₂ introduced at ambient temperature (Table 3). Two reactions were performed at a higher temperature of 440 °C. The slurry phase catalysts, MoNaph and FeNaph with excess sulfur, were used individually and as a mixture. Three different solvents, each produced with one of the three different first stage catalysts, were employed in the second stage reaction.

Catalyst type strongly affected the conversion and product distribution of the second stage reaction. The reactions that contained only MoNaph as the catalyst resulted in higher conversions than the reactions with either FeNaph or the combination of the two catalysts. The highest conversions were achieved with the HZSM-5 produced solvent and MoNaph, yielding 93.7%. The next highest conversion, 88.2%, occurred using the Low Alumina produced solvent and with MoNaph. The MoNaph catalyst also gave the highest production of hexane soluble materials, yielding 42.5% in the HZSM-5 produced solvent and 39.9% in Low Alumina produced solvent. Since half of the material that was introduced into the reactor was the hexane soluble fraction of the plastics mixture and since the hexane soluble materials present after reaction was less than half of the material that was charged, the plastics mixture converted to other fractions during reaction. The most likely products produced from the reaction of these plastics oils was gas; however, in the case of Low Alumina produced solvent, the sum of gas produced and the hexane solubles was greater than 50% of the product, indicating that some of these products were produced from coal.

Comparison of the two second stage catalysts showed that regardless of the first stage solvent used, less conversion of coal to THF soluble material was achieved with FeNaph and excess S than with MoNaph and excess S. The largest difference was observed with the solvent produced with HZSM-5 which produced a conversion of 66.6% compared to 93.7% with MoNaph. The hexane soluble yields were also less with FeNaph with all of the first stage solvents than with MoNaph. Combining MoNaph and FeNaph in the second stage resulted in nearly equivalent conversion to MoNaph with the Low Alumina solvent and somewhat less conversion with the HZSM-5 solvent. The most notable difference observed between the combined and single catalysts was the product distribution. The combined catalyst produced an extremely high yield of THF soluble materials indicating that although the reactants were converted from solids to THF soluble material, little upgrading to hexane solubles occurred. In fact, both the hexane solubles yield and the gas make were low with the combined catalyst compared to either individual catalyst.

Comparison of One-Step and Two Step Coprocessing. Comparisons of one stage and two stage coprocessing of coal and base plastics mixture are given in Figures 1 to 3. In each of these figures a comparison of the product distributions, in terms of gas, hexane solubles, THF solubles and IOM, are given for four reactions. The reactions are (1) a single stage reaction of waste plastics and coal without a solvent; (2) a single stage reaction of waste plastics and coal with 30% tetralin in hexadecane solvent; (3) a two stage reaction using first stage solvent with coal and FeNaph in the second stage; and (4) a two stage reaction using first stage solvent with coal and MoNaph in the second stage. The product distributions from the two stage reactions given in the figures are the combined product distributions from both stages.

The two stage reactions produced an improved overall product slate for the coprocessing reactions than the single stage reactions reacted with or without solvent. The two stage reaction with either FeNaph or MoNaph as the catalyst produced more hexane soluble and THF soluble yields and less IOM for two of the first stage solvents (HZSM-5 and Low Alumina) than the single stage reactions. For the Super Nova-D solvent, more hexane solubles and less IOM were produced with the two stage reactions while more gas and THF solubles were produced with the single stage reaction.

CONCLUSIONS

Increased conversion and hexane soluble yields with the two stage reactions clearly point to the advantage of two stage processing of coal and waste plastics. The predissolution of the waste plastic prior to contacting coal and the ability to tailor the catalysts and the reaction conditions specifically to the materials being reacted enhanced the reactivity of the system and promoted the desired end products.

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Table 1. Product Distribution from Two-Stage Plastics and Coal Liquefaction Reactions

Stage Number and Conditions	Product Distribution (%)		
	Catalyst	HZSM-5	Low Alumina
Stage 1 ^a Base Plastic Mixture	Gas	15.4±0.7	17.9±0.1
	Hexane Solubles	75.3±0.2	66.4±0.3
	THF Solubles	4.4±0.5	4.1±0.0
	IOM ^c	4.9±0.1	11.6±0.2
	Conversion (%)	95.1±0.1	88.4±0.2
Stage 2 ^a Coal Added to reacted Base Plastic Mixture	Gas	32.5±0.5	29.7±0.2
	Hexane Solubles	22.8±0.2	23.5±1.0
	THF Solubles	2.2±0.7	1.1±1.7
	IOM	42.5±0.4	45.1±1.4
	Conversion (%)	57.5±0.4	54.9±1.4
	Recovery (%)	71.4	74.8

^a Stage 1 reaction conditions and charge: 440 °C, 2.8 MPa of H₂ and 30 min, 2 g of base plastic mixture and 10% catalyst based on plastic charge.

^b Base plastic mixture: 50% HDPE, 30% PET and 20% PS.

^c IOM: insoluble organic matter, that is ash- and moisture-free

^d Second stage reaction conditions and charge: 2 g of coal at 400 °C, 5.6 MPa initial H₂ pressure for 30 min.

Table 2. Product Distribution from Catalytic Liquefaction of Base Plastics Mixture^{a,b}

Catalyst	Catalyst		
	Low Alumina	Super Nova-D	HZSM-5
Gas	17.9±0.1	14.9±0.1	15.2±0.7
Hexane Solubles	66.4±0.3	75.1±0.4	75.5±0.2
THF Solubles	4.1±0.0	4.5±0.5	4.4±0.5
IOM ^c	11.6±0.2	5.5±0.8	4.9±0.1
Conversion (%)	88.4±0.2	94.5±0.8	95.1±0.1
Recovery (%)	73.9	70.8	71.8

^a Reaction Conditions: 440 °C, 60 min and 2.8 MPa of H₂ introduced at ambient. 2 g of base plastic mixture and 10% catalyst based on plastic charge; no additional solvent was added.

^b Base plastic mixture: 50% HDPE, 30% PET and 20% PS.

^c IOM: insoluble organic matter.

Table 3. Product Distribution from Second Stage Coal Liquefaction Reactions using Hexane Soluble Plastic Oil as Solvent^{a,b}

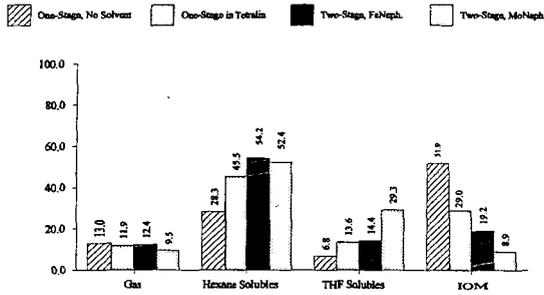
Reaction Temperature	First Stage Catalyst and Charge	Second Stage Catalyst ^c	Product Distribution, %				Conversion (%)	Recovery (%)
			Gas	Hexane Solubles	THF Solubles	IOM		
400 °C	HZSM-5+Base Plastics	1000 ppm Mo	8.0±0.3	42.5±0.5	43.2±1.0	6.3±0.2	93.7±0.2	81.7±3.7
400 °C	HZSM-5+Base Plastics	1000 ppm Fe	9.5±0.8	32.8±0.4	24.3±3.2	33.4±2.8	66.6±2.8	81.4±2.2
400 °C	HZSM-5+Base Plastics	500 ppm Mo 500 ppm Fe	3.8±0.1	29.2±1.1	54.2±2.4	12.9±3.6	87.1±3.6	88.7±1.3
400 °C	Low Alumina+ Base Plastics	1000 ppm Mo	19.9±0.6	39.9±1.1	28.3±0.6	11.8±0.0	88.2±0.0	72.2±1.5
400 °C	Low Alumina+Base Plastics	1000 ppm Fe	23.0±0.0	29.6±0.9	19.3±0.1	28.1±0.7	71.9±0.7	74.6±2.4
400 °C	Low Alumina+Base Plastics	500 ppm Mo 500 ppm Fe	3.6±0.7	19.2±2.6	64.6±0.1	12.6±1.9	87.4±1.9	92.6±2.0
440 °C	Low Alumina+Base Plastics	1000 ppm Mo	49.7±1.2	8.4±5.2	6.1±1.2	35.9±2.7	64.1±2.7	75.9±1.2
440 °C	Low Alumina+Base Plastics	1000 ppm Fe	46.9±0.1	0.5±1.4	4.0±0.8	48.7±0.7	51.3±0.7	81.8±1.3
400 °C	Super Nova-D+ Base Plastics	1000 ppm Mo	35.7±0.1	27.2±0.0	10.0±0.1	27.1±0.3	72.9±0.3	67.5±0.6
400 °C	Super Nova-D+ Base Plastics	1000 ppm Fe	33.5±0.1	18.5±0.5	5.3±0.5	42.8±0.9	57.2±0.9	69.1±0.3

^a Reaction Conditions: 400 °C, 30 min, 5.6 MPa H₂ introduced at ambient temperature, and 2 g of coal and 2 g of plastic oil were added to the reactor.

^b Solvent was from base plastic mixture (HDPE:PET:PS=50:30:20), which was liquefied at 440 °C, 2.8 MPa of H₂ for 60 min.

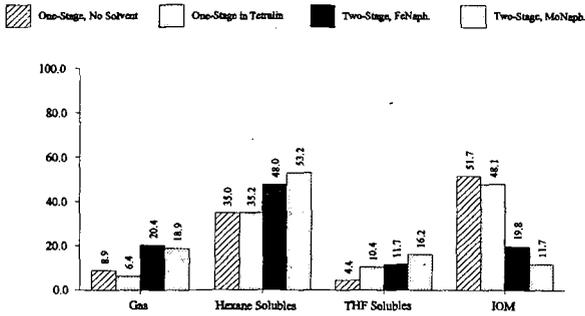
^c Catalyst contained 1000 ppm Mo or Fe naphthenate plus 6000 ppm S. When combined catalysts were used, 500 ppm Fe and 500 ppm Mo plus 6000 ppm S were added to the reactor.

Figure 1. Comparison of One-Stage and Two-Stage Coprocessing of Coal and Base Plastic Mixture Using HZSM-5



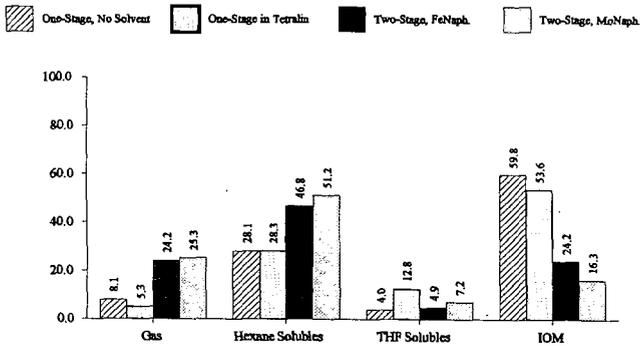
a. One-stage coprocessing: coal + base plastic mixture at 440°C.
 b. Two-stage coprocessing: coal + base plastic oil at 400°C.

Figure 2. Comparison of One-Stage and Two-Stage Coprocessing of Coal and Base Plastic Mixture Using Low Alumina



a. One-stage coprocessing: coal + base plastic mixture at 440°C.
 b. Two-stage coprocessing: coal + base plastic oil at 400°C.

Figure 3. Comparison of One-Stage and Two-Stage Coprocessing of Coal and Base Plastic Mixture Using Super Nova-D



a. One-stage coprocessing: coal + base plastic mixture at 440°C.
 b. Two-stage coprocessing: coal + base plastic oil at 400°C.